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THE SOFTENING RATE OF A STEEL WHEN TEMPERED FROM DIFFERENT INITIAL STRUCTURES

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Abstract

This paper deals with the softening characteristics of a typical carbon steel, containing 0.94 per cent carbon and 0.40 per cent manganese, when heat treated to four different initial structural states and thereafter tempered for a period ranging from 2 seconds to 22 hours at five different temperatures: 600, 900, 1050, 1200 and 1300 degrees Fahr. The four initial states were martensite, bainite, fine nodular pearlite, and coarse pearlite.

In general, the larger the size of the carbide particles in the initial structure, the lower is the rate of softening during tempering. At any given temperature the coarse lamellar structure softens most slowly, and after 22 hours at the higher temperatures this structure is even slightly harder than the martensite similarly tempered. At the lower temperatures the difference in hardness, in terms of Brinell number, between martensite and bainite is nearly independent of tempering time after a brief initial period. The fact that the two curves are nearly parallel, when time is expressed on a logarithmic scale, does not imply that bainite and martensite soften identically for equal time intervals. At the higher temperatures the four tempered structures approach a common hardness, which gradually decreases with increased tempering time.

ALMOST all heat treatments of steel employed to obtain high strength and toughness involve quenching, or at least relatively rapid cooling, from a temperature at which the steel is in the austen-

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itic condition, followed by tempering at a temperature lower than that at which austenite would be regenerated. To set up a suitable tempering schedule for a given steel in a given structural state it is necessary to know something of the characteristic rate of softening of that steel. For instance, many hardened alloy steels—particularly those containing strongly carbide-forming elements such as molybdenum, tungsten, vanadium, titanium, and chromium—require a relatively high tempering temperature, or a long time at temperature, to reduce the hardness to a given level; and at a given temperature, such alloy steels soften less rapidly than a plain carbon steel of comparable carbon content. Moreover, in the same steel, the several structures soften at different rates during tempering, and the relative rates may change with temperature. Accordingly, the systematic study of the behavior of steel during tempering is receiving increased attention from metallurgical investigators as indicated by two recent papers by Austin and Norris (1), (2).[1] Bain and co-workers have made numerous references to the subject, particularly with respect to the influence of alloying elements on tempering behavior (3), (4), (5), (6), (7), and Epstein, in his monograph on the constitution of alloys of iron and carbon (8), devoted a whole chapter to the subject of tempering.

This paper deals with the softening rates of martensite, bainite (the dark-etching, acicular product of austenite transformation), fine nodular pearlite, and moderately coarse pearlite, all direct transformation products of austenite as developed in a single steel, the composition of which was: C 0.94%; Mn 0.40%; Si 0.133%; P 0.034%; S 0.044%

Procedure

Small specimens ($\frac{1}{10}$ x $\frac{3}{16}$ x 1¼ inch) were treated as outlined in Table I to obtain the four different initial structures, which are illustrated in the representative photomicrographs at × 2500, Fig. 1.

Specimens of each of these four structures were tempered in lead at 600, 900, 1050, 1200 and 1300 degrees Fahr. for a period of time ranging from 2 seconds to 80,000 seconds (approximately 22 hours), except that the coarse pearlite series was tempered only at 1200 and 1300 degrees Fahr. A separate specimen was used for each time-temperature combination of tempering; i.e., no cumulative tempering was employed. At the end of the tempering treatment each

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

specimen was cooled in water at room temperature. Sufficient material was removed by grinding to eliminate decarburization; ten Rockwell C hardness readings were then recorded for each specimen and the average converted to the Brinell number. The results are presented in Tables II to VI and in the form of curves (Figs. 3 to 7) in which Brinell hardness is plotted as ordinate, and tempering time,

Table I
Initial Structures and Corresponding Heat Treatments Employed

	Description	Rockwell C	Brinell	Heat Treatment
Structure Martensite (M)	Characteristic structure of fully hardened steel; obtained by quenching austenite.	65	682	10 mins. in lead 1500 degrees Fahr.; quenched in brine.
Bainite (B)	Acicular, dark-etching product of constant temperature transformation of austenite at temperatures between about 900 and 300 degrees Fahr.	53.5	534	10 mins. in lead 1500 degrees Fahr.; rapidly transferred to lead-bismuth bath at 600 degrees Fahr. and held 30 mins.;* cooled in water.
Fine Nodular Pearlite (FP)	Fine lamellar product of contures between about 1150 and tion of austenite at tempera- 900 degrees Fahr. Could also stant-temperature transforma- be obtained by moderately rapid cooling of austenite.	44.5	429	10 mins. in lead 1500 degrees Fahr.; rapidly transferred to lead bath at 900 degrees Fahr. and held 30 seconds;* cooled in water.
Coarse Pearlite (P)	Coarse lamellar product of constant-temperature transformation of austenite at temperatures between the lower critical or A_1 temperature and about 1150 degrees Fahr. Could also be obtained by moderately slow cooling of austenite.	33	311	10 mins. in lead 1500 degrees Fahr.; rapidly transferred to lead bath at 1225 degrees Fahr. and held 40 seconds;* cooled in water.

*This period was used to insure complete isothermal transformation of this steel at this temperature.

on a logarithmic scale, as abscissa. The logarithmic scale was used merely as a matter of convenience and its peculiarities should be kept in mind in the interpretation of the charts in this paper.

In addition to the hardness measurements, a large number of the specimens were examined microscopically. The structural changes observed on tempering confirm the widely held view that the softening of steel brought about by tempering is due largely to a gradual coalescence of the carbide particles. In Fig. 1 micrographs at $\times$ 2500 of the four initial structures are reproduced for comparison with the micrographs at $\times$ 1000 in Fig. 2 of the characteristic structure which each type of specimen reached after 22 hours tempering at 1300 degrees Fahr.

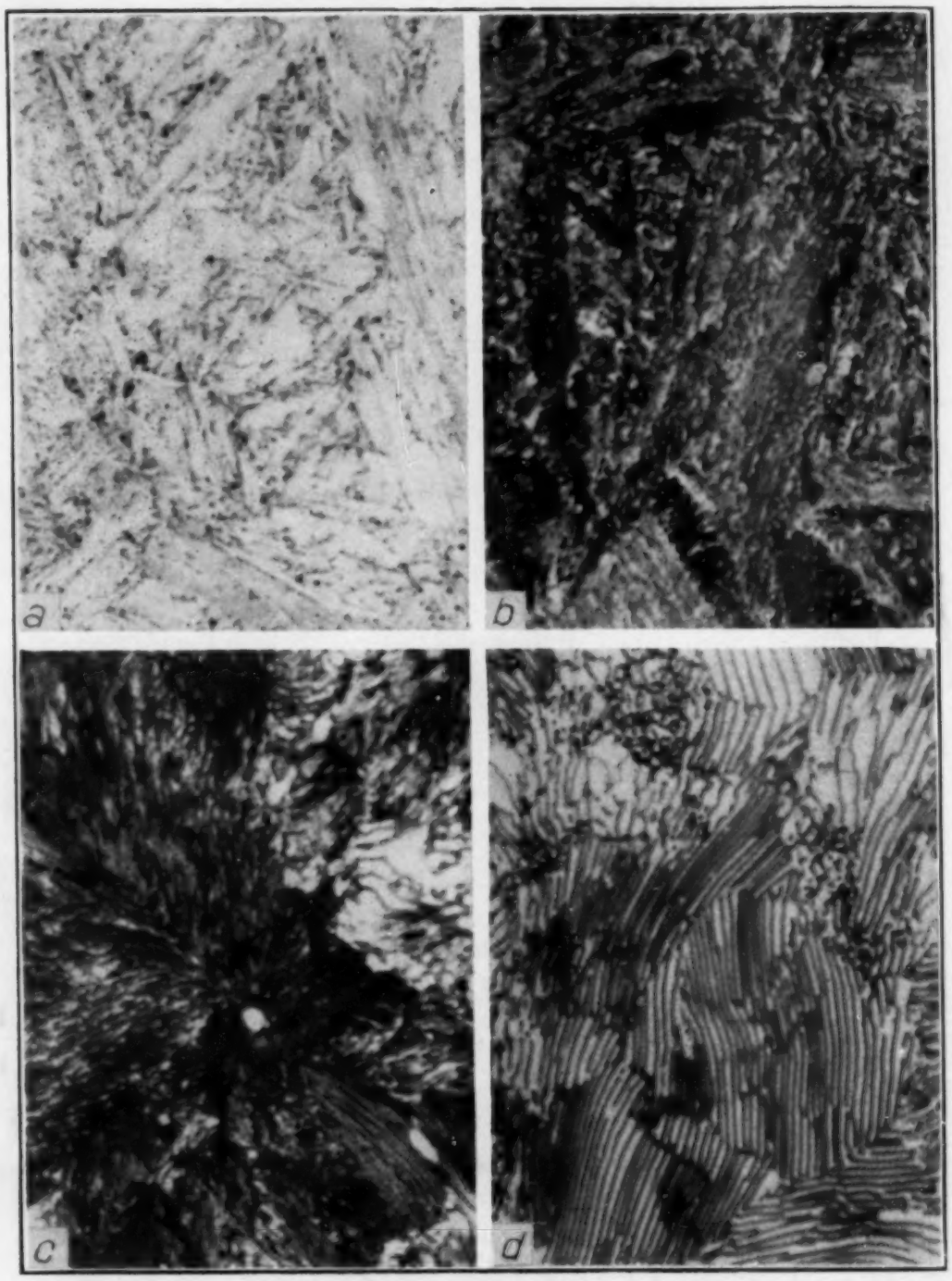


Fig. 1—Initial Structures Before Tempering. × 2500.
Fig. 1a—Martensite—Hardness: RC 65 (BHN 682).
Fig. 1b—Bainite—Hardness: RC 53.5 (BHN 534).
Fig. 1c—Fine Pearlite—Hardness: RC 44.5 (BHN 429).
Fig. 1d—Medium Coarse Pearlite—Hardness: RC 33 (BHN 311).

Discussion of Results

All the structures soften more rapidly as the tempering temperature is raised, in line with the greater solubility and diffusivity

Table II
Hardness Changes Brought About by Tempering at 600 Degrees Fahr.

Time at 600 Degrees Fahr. Seconds	Initial Structure Before Tempering: Martensite RC	Martensite BHN†	Bainite RC	Bainite BHN†	Fine Pearlite RC	Fine Pearlite BHN†
0	64.8*	682	53.3*	534	45.7*	444
2	64.4	682	53.2	534	45.8	444
5	62.0	653	53.5	534	45.9	444
10	61.4	627	53.5	534	46.5	444
20	61.0	627	53.6	534	46.2	444
40	59.3	601	53.2	534	46.1	444
80	59.6	601	53.7	534	45.8	444
160	59.1	601	53.6	534	46.0	444
320	58.4	601	53.3	534	46.2	444
640	57.5	578	53.2	534	46.1	444
1200 (20 min.)	57.0	578	52.4	514	46.0	444
2400	55.7	555	52.1	514	45.9	444
4800 (80 min.)	55.4	555	52.5	514	45.3	429
10,000	54.0	534	51.5	514	44.9	429
20,000 (5½ hr.)	53.0	534	51.1	495	45.2	429
40,000	53.0	534	50.5	495	45.6	429
80,000 (22 hr.)	51.5	514	50.0	495	44.1	415

*Initial hardness before tempering.
†BHN converted from Rockwell C value.

Table III
Hardness Changes Brought About by Tempering at 900 Degrees Fahr.

Time at 900 Degrees Fahr. Seconds	Initial Structure Before Tempering: Martensite RC	Martensite BHN†	Bainite RC	Bainite BHN†	Fine Pearlite RC	Fine Pearlite BHN†
0	65.6*	682	54.2*	534	45.6*	429
2	60.2	627	53.7	534	45.1	429
5	52.0	514	47.5	461	45.6	429
10	50.7	495	46.9	444	45.4	429
20	48.7	477	45.4	429	45.3	429
40	47.7	461	44.0	415	45.0	429
80	46.5	444	43.4	415	43.8	415
160	45.7	444	42.6	401	43.3	415
320	44.8	429	41.3	388	43.2	415
640	43.9	415	39.5	375	42.9	401
1200 (20 min.)	42.5	401	39.4	363	42.0	401
2400	41.5	388	....	...	41.1	388
4800 (80 min.)	40.5	375	37.6	352	40.1	375
10,000	39.4	363	....	...	38.7	363
20,000 (5½ hr.)	38.3	352	35.4	331	37.8	352
40,000	37.1	341	....	...	35.9	331
80,000 (22 hr.)	35.9	331	33.4	311	34.9	321

*Initial hardness before tempering.
†BHN converted from RC value.

of carbon in ferrite at the higher temperatures. At all five temperatures the martensite loses hardness, in terms of Brinell number, considerably faster during the first few seconds than any of the other three initial structures. In all cases the curve for Brinell number against tempering time, the latter on a logarithmic scale, becomes nearly straight; but it is to be noted that this means a nearly constant rate of softening for equal increments of the logarithm of time. For example, on the curve for 900 degrees Fahr. the drop in Brinell hardness number in the interval 100 to 1000

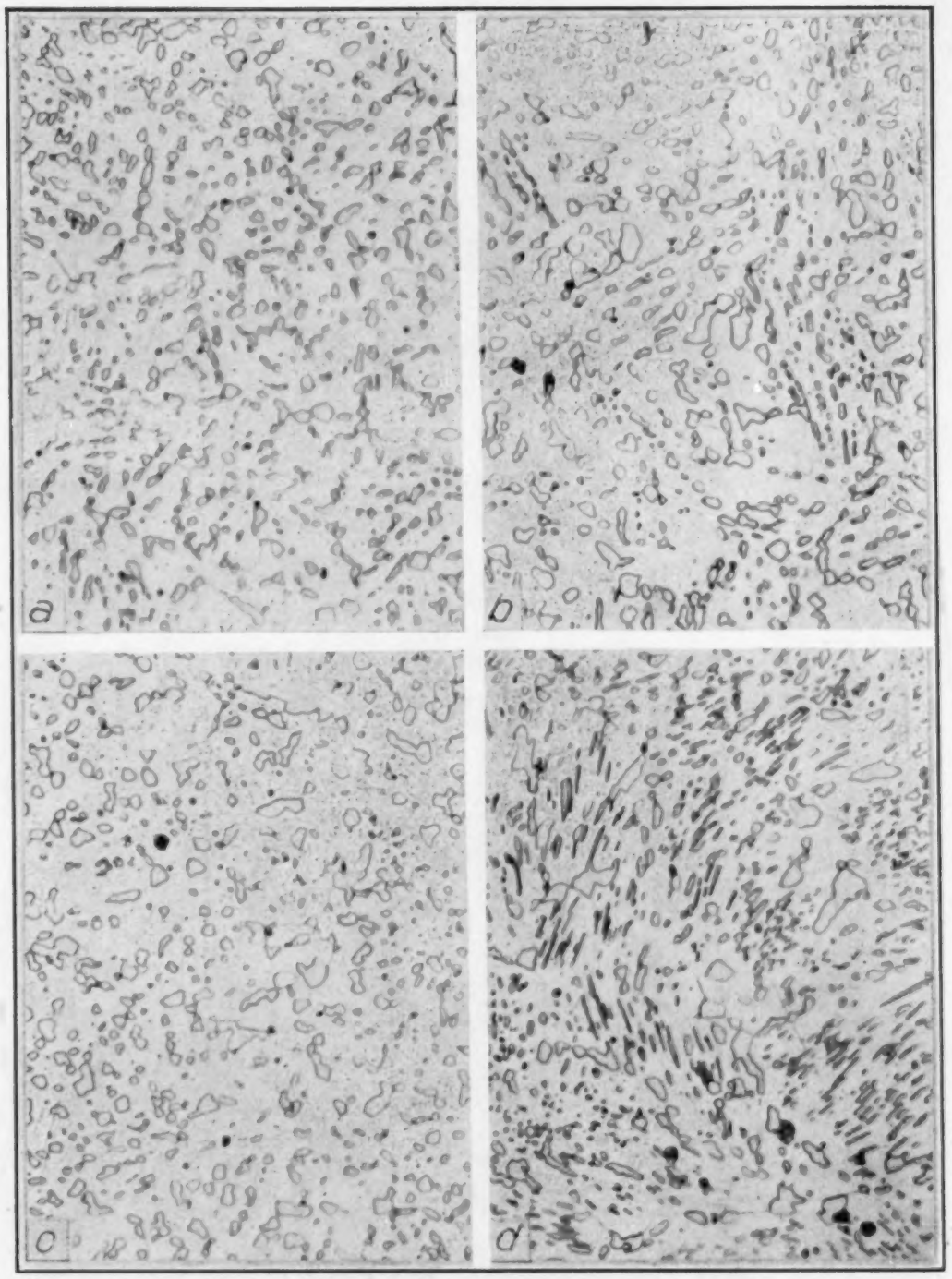


Fig. 2—Structures After Tempering 22 Hours at 1300 Degrees Fahr. × 1000.
Fig. 2a—Initially Martensite—Hardness: RC 10 (BHN 179).
Fig. 2b—Initially Bainite—Hardness: RC 8.5 (BHN 174).
Fig. 2c—Initially Fine Pearlite—Hardness: RC 10 (BHN 179).
Fig. 2d—Initially Medium Coarse Pearlite—Hardness: RC 11.5 (BHN 183).

seconds is 40 points, that in the interval 1000 to 10,000 seconds is again 40 points, these two intervals being *equal on the chart*, but representing *actual times* in a ratio of 1 to 10. Thus a nearly straight

line on the logarithmic scale of time corresponds to a continually decreasing softening rate as ordinarily reckoned in terms of equal increments of time. Likewise, the approximate parallelism of the curves for martensite and bainite shows that the drop in Brinell

Table IV
Hardness Changes Brought About by Tempering at 1050 Degrees Fahr.

Time at 1050 Degrees Fahr. Seconds	Initial Structure Before Tempering: Martensite RC	Martensite BHN†	Bainite RC	Bainite BHN†	Fine Pearlite RC	Fine Pearlite BHN†
0	64.9*	682	54.2*	534	45.0*	429
2	57.1	578	45.4	429	45.0	429
5	46.6	444	42.4	401	43.0	401
10	44.5	429	41.9	401	42.1	401
20	43.3	415	40.5	375	41.6	388
40	42.3	401	39.7	375	40.3	375
80	40.5	375	38.1	352	39.5	375
160	39.5	375	36.9	341	38.0	352
320	38.6	363	36.1	331	37.1	341
640	37.3	352	34.4	321	35.9	331
1200 (20 min.)	35.5	331	33.7	311	35.7	331
5000 (83 min.)	32.4	302	31.0	293	33.0	311
20,000 (5½ hr.)	30.1	285	28.9	277	30.6	285
80,000 (22 hr.)	27.5	262	26.3	255	27.9	269

*Initial hardness before tempering.
†BHN converted from RC value.

Table V
Hardness Changes Brought About by Tempering at 1200 Degrees Fahr.

Time at 1200 Degrees Fahr. Seconds	Initial Structure Before Tempering: Martensite RC	Martensite BHN†	Bainite RC	Bainite BHN†	Fine Pearlite RC	Fine Pearlite BHN†	Pearlite RC	Pearlite BHN†
0	64.3*	682	52.5*	514	44.0*	415	33.6*	311
2	46.8	444	41.7	388	43.0	401	....	...
5	39.7	375	38.1	352	40.6	375	....	...
10	38.6	363	35.9	331	38.7	363	....	...
20	36.2	341	34.7	321	37.0	341	....	...
							50 sec.	
40	34.7	321	33.3	311	35.7	331	31.2	293
							100 sec.	
80	33.3	311	31.4	293	34.2	321	31.3	293
160	31.3	293	30.3	285	32.7	302	....	...
320	30.2	285	28.8	277	31.2	293	29.3	277
640	28.7	269	27.9	269	29.2	277	....	...
1200 (20 min.)	27.4	262	26.4	255	29.0	277	28.6	269
2400	24.8	248	24.9	248	26.1	255	...	...
4800 (80 min.)	23.2	235	22.8	235	25.3	248	26.2	255
10,000	20.2	223	20.2	223	22.0	229	....	...
20,000 (5½ hr.)	17.7	207	18.9	217	20.7	223	21.1	223
40,000	15.6	201	15.5	201	17.2	207	....	...
80,000 (22 hr.)	13.6	192	13.3	192	15.0	197	17.1	207

*Initial hardness before tempering.
†BHN converted from RC value.

number is about the same for both in equal time intervals when these intervals are measured from the same value of time as a starting point, but not for equal time intervals measured from different times as starting points. This difference can be stated in another way, as in the following example. At 900 degrees Fahr. the hard-

ness of martensite, initially BHN 680, drops to 500 BHN in about 10 seconds, and to 350 BHN in about 500 minutes; whereas that of bainite, initially 535 BHN, reaches 500 BHN in about 3 seconds and 350 BHN in about 80 minutes. Thus a difference of only 7 seconds in the time required to reach 500 BHN increases to 7 hours when we consider the 350 BHN level.

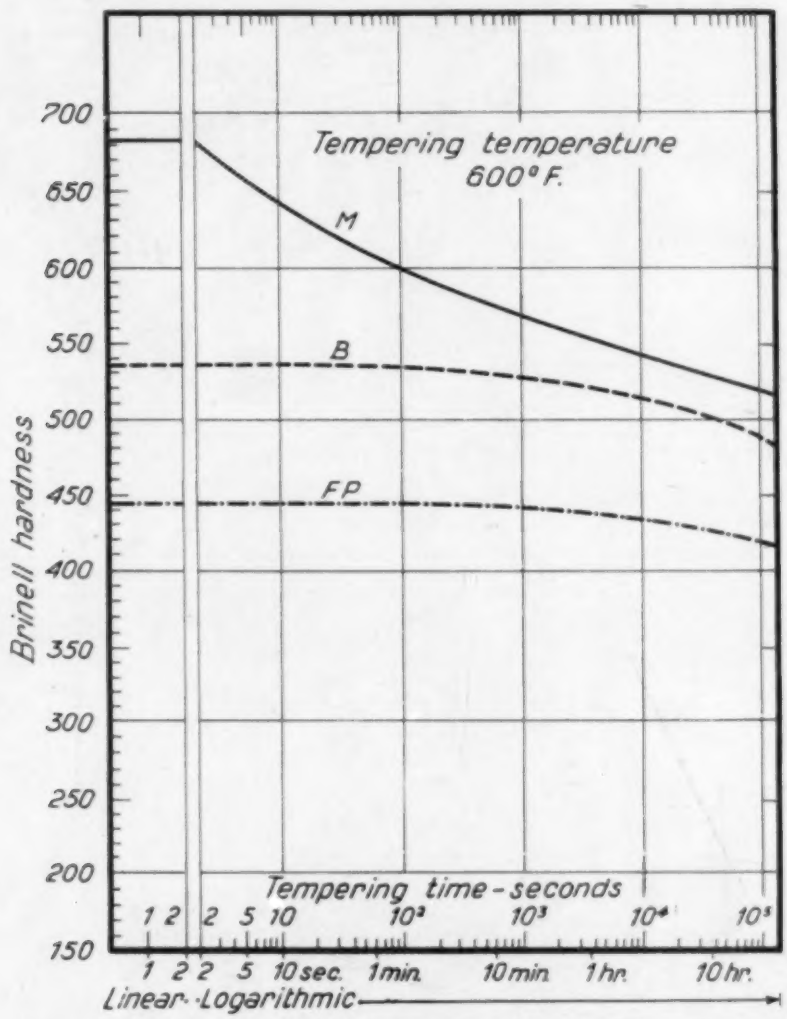


Fig. 3—Hardness Curves for Steel Tempered at 600 Degrees Fahr.

The curves for the high temperatures, 1200 and 1300 degrees Fahr., show most clearly that the softer structures soften more slowly than the harder. It appears that the hardness number at which the curves of any two of these structures intersect is nearly independent of the tempering temperature. For instance, the curves for martensite and for fine pearlite intersect at a hardness not far from 350 BHN at each of the four higher temperatures, but only

after a time interval which is longer the lower the temperature. Beyond the intersection the pearlite remains somewhat harder than the tempered martensite, both continuing to soften thereafter at a

Table VI
Hardness Changes Brought About by Tempering at 1300 Degrees Fahr.

Time at 1300 Degrees Fahr. Seconds	Initial Structure Before Tempering — Martensite RC	Martensite BHN†	Bainite RC	Bainite BHN†	Fine Pearlite RC	Fine Pearlite BHN†	Pearlite RC	Pearlite BHN†
0	64.7*	682	52.5*	514	43.0*	401	32.7*	302
2	40.6	375	35.9	331	40.4	375	....	...
5	35.0	321	35.2	331	38.0	352	....	...
10	33.1	311	32.1	302	34.3	321	32.2	302
20	31.0	293	30.8	285	32.3	302	....	...
40	29.1	277	28.4	269	31.4	293	30.9	293
80	26.9	262	26.2	255	29.0	277	28.5	269
160	25.9	255	25.1	248	27.7	262	27.1	262
320	23.8	241	22.9	235	24.9	248	25.3	248
640	22.7	235	20.8	223	23.0	235	....	...
1200 (20 min.)	20.9	223	19.5	217	21.5	229	23.7	241
5000 (83 min.)	19.2	217	17.6	207	20.1	223	19.9	217
20,000 (5½ hr.)	14.0	192	14.2	197	15.2	197	15.2	197
80,000 (22 hr.)	9.8	179	8.6	174	9.8	179	11.4	183

*Initial hardness before tempering.
†BHN converted from RC value.

decreasing rate. The practical significance of this is that a section of quenched steel which has failed to harden throughout and thus has a fine pearlitic core, may be brought to a uniform hardness throughout the cross section by holding it for an appropriate time, which will be quite short if the temperature is high. In fact, if tempering is continued beyond the time required for the martensitic case and the pearlitic core to reach a common hardness, the case will become softer than the core because of the lower softening rate of the pearlitic structure in the core. Thus the familiar U-shaped curve representing the hardness distribution in a quenched cylinder can be flattened out and even inverted by proper selection of the time-temperature conditions of tempering. To illustrate this, a cylinder, 2¼ inches long and $\frac{15}{16}$ inch in diameter, of a 0.74 per cent carbon steel was quenched from 1700 degrees Fahr. and fractured midway between the ends. After grinding and polishing the fractured surface of one of the halves, the hardness distribution across several diameters of the piece was recorded; the piece was then tempered at 1200 degrees Fahr. for 20, 50 and 100 seconds, and the hardness distribution across the section again measured after each tempering period. The results, shown graphically in Fig. 8, were as anticipated.

In general, microscopic examination confirmed the results of

the hardness measurements. After 22 hours at 1200 or 1300 degrees Fahr. all four initial structures are so well spheroidized that differences in structure have become very slight indeed. After 22

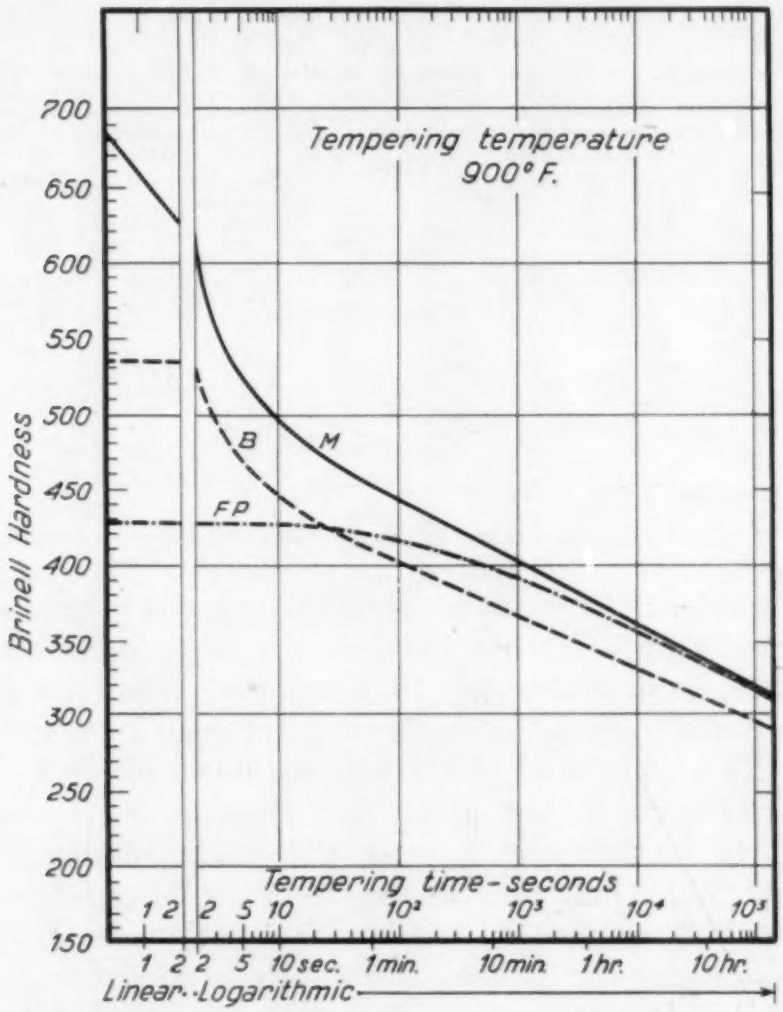


Fig. 4—Hardness Curves for Steel Tempered at 900 Degrees Fahr.

hours at 1300 degrees Fahr., such differences as there are indicate that the carbide particles in specimens initially martensitic are most uniform in size and most spheroidal in shape, while the carbides in specimens initially fine pearlitic appear to be most uniformly distributed. Thus our experience indicates that when a well spheroidized uniform structure is desired in a steel, it is advantageous to start from either martensite or fine pearlite. Traces of lamellar structure are still plainly evident after 22 hours at 1300 degrees Fahr. in specimens which were initially coarse pearlite.

The similarity in initial softening behavior of martensite and

bainite, particularly by contrast with that of pearlite, and the nearly constant difference in hardness number between martensite and bainite on tempering for equal times suggest that, in structure, bain-

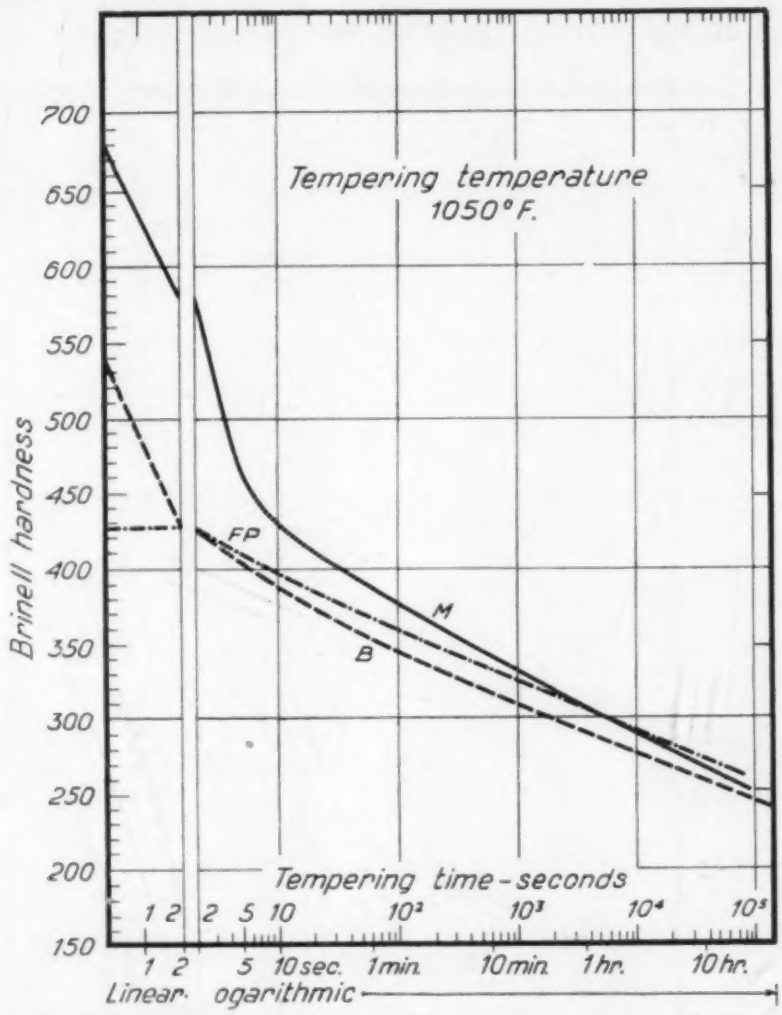


Fig. 5—Hardness Curves for Steel Tempered at 1050 Degrees Fahr.

ite resembles martensite rather than fine pearlite. If martensite is an atomic or molecular dispersion of carbon or carbide, bainite may perhaps be regarded as a dispersion of groups or aggregates of carbide. This tentative view is in line with the well known fact that the greater the degree of supersaturation of a phase at the moment it is precipitated—in this case, therefore, the lower the temperature at which it is formed—the finer will be the particles precipitated. In this connection it may be noted, moreover, that finer particles, because of their greater interfacial area, not only dissolve more rapidly, but also have a higher real solubility than coarser particles

of the same substance. In other words, there is always a tendency for particles to coarsen, by reason of this difference in real solubility between finer and coarser particles. The rate of this coarsening process, however, under many circumstances may be so small as to be inappreciable; but, if other things are equal it will be

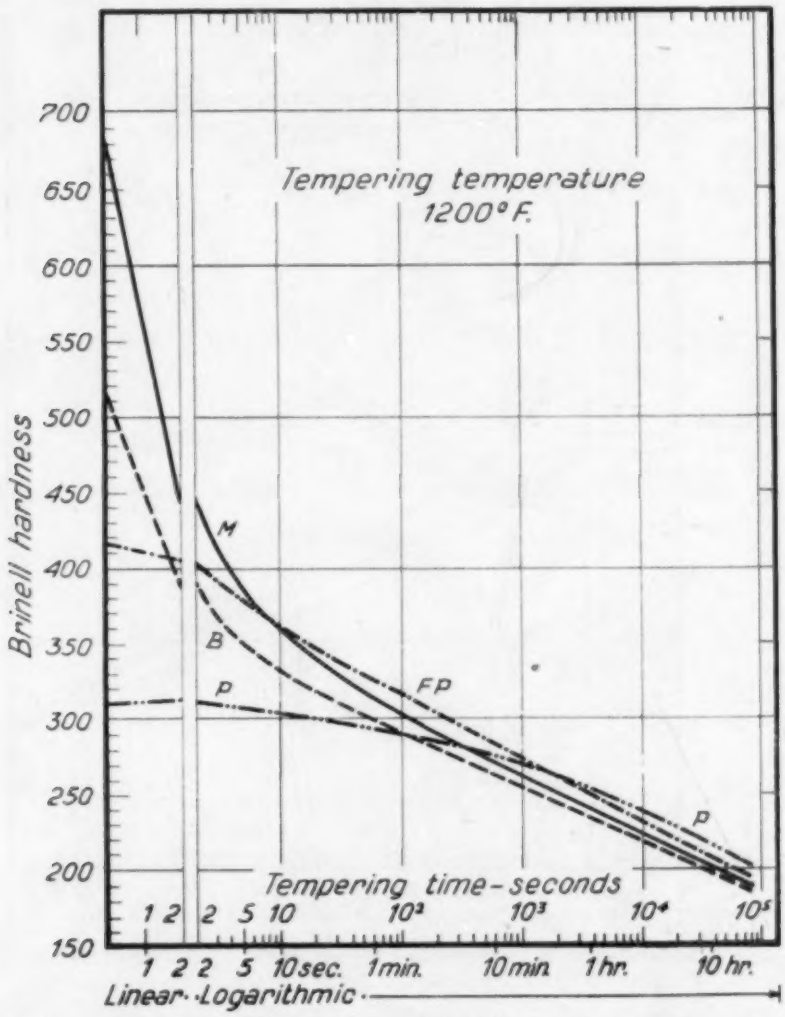


Fig. 6—Hardness Curves for Steel Tempered at 1200 Degrees Fahr.

greater the finer the particle, and greater the higher the temperature because, presumably, of the rapid increase of rate of diffusion with rise in temperature. Thus the rapid initial softening of martensite and bainite would be expected if the picture of their structure sketched above is right.

When the steel is pearlitic, the total interfacial area is, presumably, smaller than when the steel is in the form of bainite; correspondingly the coarsest pearlite tempers most slowly. The car-

bide lamellæ appear first slowly to thicken and change into short rods or disks, and later to coalesce gradually to larger and more spheroidal particles. As the size of the carbide particles increases, their difference in solubility, which is the underlying cause of the coalescence, becomes less and less; moreover the distance between

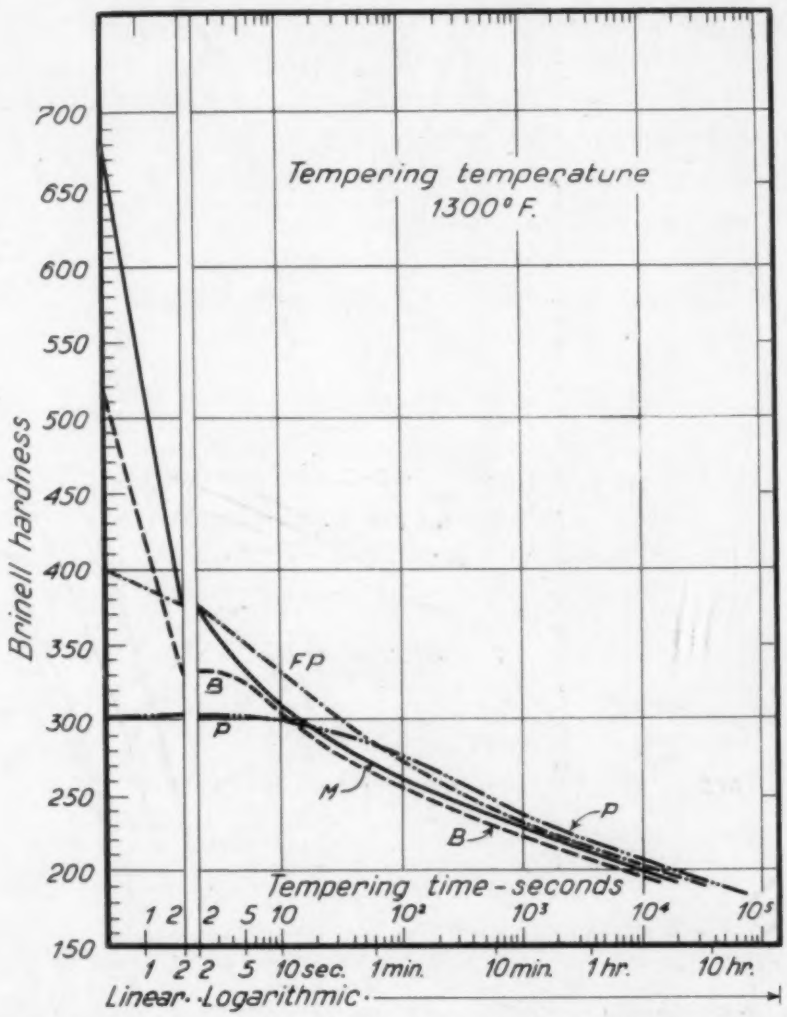


Fig. 7—Hardness Curves for Steel Tempered at 1300 Degrees Fahr.

particles increases, so that the rate of the process is affected by both these factors and thus decreases continually, so that what is, in effect, a stationary state is reached in a few hours. From long-time spheroidizing treatments, such for example, as holding a specimen at a temperature just below the A_{e1} point for as long as 300 hours, it was found that the carbides assume a size and shape which is only slightly larger and more spheroidal than that attained after 22 hours at 1200 or 1300 degrees Fahr. In other words, after

reaching a certain size, the particles grow at a vanishingly small rate, in accord with general experience of analogous cases. Thus as the time of tempering is increased, the softening curves for the different structures of the same steel tend to converge into a single

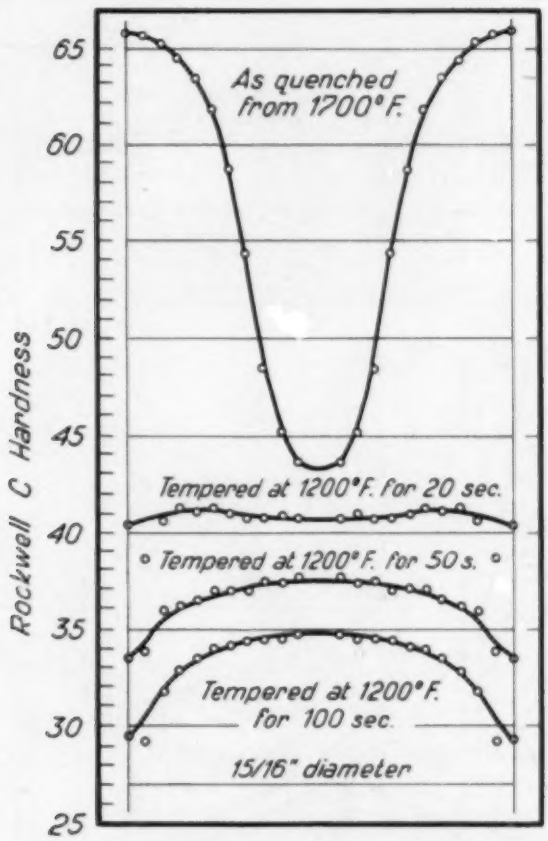


Fig. 8—Hardness Distribution Across a 0.74% C Steel Cylinder in the As-Quenched Condition and After Three Different Tempering Treatments.

curve which becomes more and more nearly horizontal even when the time-scale is logarithmic.

Summary

1. The rate of softening during tempering of a typical carbon steel is dependent upon the initial structure of the steel prior to tempering.

2. In general, the finer the state of dispersion of the carbide particles in the structure before tempering, the faster will the Brinell hardness number decrease during tempering. Of the structures examined—martensite, bainite, fine pearlite, and coarse pearlite—

the last named is distinctly the slowest to soften at any given temperature.

3. The rate of softening of martensite is so much faster than that of pearlite that the two curves for hardness vs. tempering time at a given temperature actually cross. Thus, under appropriate tempering conditions, the fully-hardened (martensitic) surface region of a section of quenched steel which failed to harden all the way through may be made softer than the relatively soft (pearlitic) core which did not harden on quenching.

4. After a brief initial period, the difference in Brinell number of martensite and bainite on tempering remains nearly constant.

5. At the high tempering temperatures the four initially different structures investigated tend to approach a common hardness which decreases more and more slowly with increased time at temperature.

Acknowledgments

The author acknowledges his obligation to Dr. E. C. Bain, who suggested this investigation, and the assistance of Dr. B. R. Queneau who carried out many of the preliminary experiments leading up to the results described.

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DISCUSSION

Written Discussion: By S. C. Spalding, metallurgical engineer, American Brass Co., Waterbury, Conn.

The author has added some interesting and valuable data to the information on what happens to a carbon steel when tempering various structures. In describing the procedure it is stated that Rockwell C hardness readings are taken for each specimen and the average converted to Brinell number and then these converted Brinell values plotted against tempering time to produce the curve shown in the paper.

In considering this I wonder why, if the hardness values were taken on the Rockwell scale and recorded as Rockwell numbers, the curves were not plotted in terms of Rockwell numbers versus tempering time rather than the converted Brinell. I wondered about this particularly in view of the fact that it is generally recognized that no consistent correlation can exist between various hardness testing machine scales. This means that the converted Brinells which are used in plotting the curves do not actually represent any specific hardness values.

No doubt the author has some good reason for this but it would seem, offhand, more reasonable to have plotted the effect of tempering time on the hardness values in the scale in which the actual readings were taken, where, at least, they would represent the hardness determinations made.

I would be glad to have the author inform us why the converted hardness was used in this case.

Written Discussion: By John L. Burns, mill metallurgist, Republic Steel Corp., Chicago.

Mr. Engel is to be congratulated on this clear and concise exposition of the effect of tempering a 0.94 per cent carbon steel from different initial structures. The reversion of the "U" type hardenability curve is particularly interesting and affords a good basis to judge the best beginning structures for spheroidization.

In conjunction with this part of the work, has the writer carried out any further experiments on possible faster methods of spheroidization—such as the successive raising and lowering the temperature above and below the Ac_1 point? How would this compare with the rate attained by starting with the best initial structure followed by tempering?

Written Discussion: By M. C. Fetzer, instructor in metallurgy, Pennsylvania State College, State College, Pa.

Mr. Engel has performed a valuable piece of work by comparing the softening rate of bainite with those of martensite and two pearlites. An important point is that when tempered at temperatures above their formation temperatures the various structures show little difference in hardness after a short initial time period.

The author has suggested that because bainite initially softens similarly to martensite and because after greater lengths of time the difference in hardness between bainite and martensite remains nearly constant, bainite is structurally like martensite and not fine pearlite. Mr. Engel has chosen to work with a hard 600 degrees Fahr. bainite, and therefore, as it is far removed from

the final hardness reached by all of these structures after 22 hours at the several temperatures, it like martensite, softens rapidly in the initial stages. Similarly a heavily cold-worked steel would soften rapidly in its initial stages when annealed because its hardness is far removed from the dead soft value. Had an 800 or 850-degree Fahr. bainite, having the same initial hardness of fine pearlite, been tempered instead of this 600-degree Fahr. bainite the softening curve would have been different initially and perhaps more like that of fine pearlite. It is not to be inferred from this that bainite is similar to fine pearlite, but such a conclusion could be drawn by curve comparisons as was done in this paper. Regarding the parallelism of bainite and martensite hardness curves after a brief initial period, this relationship holds equally as well for the bainite-fine pearlite curves.

Written Discussion: By A. B. Wilder, assistant professor of Metallurgical Engineering, University of Illinois, Urbana, Ill.

The influence of the size factor is of interest with reference to the results of this investigation. The author used specimens $\frac{1}{10}$ inch thick and from a practical point of view, this type of material has a limited application. Information of an indirect nature is presented in Fig. 8 and it would be of interest to have Mr. Engel present his views with reference to the behavior of thicker specimens.

Author's Reply

In regard to Mr. Spalding's discussion I quite agree that it would seem more reasonable to have plotted the effect of tempering time on the Rockwell C hardness values, the scale in which the actual readings were taken, and originally this had been done.

However, when plotting Rockwell C hardness against the logarithm of tempering time, a change in slope appeared in the lower end of the curves, making it seem as though the softening rate of all structures suddenly increased at about 20 C and lower hardnesses. This tended to obscure the points made in presenting the plots and was entirely due to the peculiarities of the Rockwell C scale in this low hardness range. Looking for an explanation, we examined the Rockwell C-Brinell relationship and found that while at higher hardnesses a straight line relationship exists, the Rockwell C hardness drops off considerably faster than the Brinell hardness in this low range.

We, therefore, converted all values to Brinell hardness numbers and obtained the plot shown in the paper in which this unreal sudden change in softening rate at low hardnesses was no longer apparent.

As to Mr. Burns' question I believe that, while I have not conducted any such experiments, the successive raising and lowering of the temperature to slightly above and below the Ac_1 point has been found to be the fastest method of spheroidization. By having the most suitable initial structure in addition to following this procedure, one would therefore be likely to obtain the most rapid and thorough spheroidization, and it would be of interest to confirm this by actual experiment.

In answer to Mr. Wilder's question I would like to state that thin specimens were purposely used to avoid any mass effect and thus to be able to bring the entire specimen to temperature almost instantly.

REACTIONS TO ANNEALING ABOVE THE EUTECTOID TEMPERATURE OF QUENCHED HYPEREUTECTOID STEELS

By Charles R. Austin and M. C. Fetzer

Abstract

A series of hypereutectoid steels of similar chemical composition has been shown, in previous researches, to react in a markedly different manner, with respect to spheroidization, graphitization and softening, on prolonged tempering of the hardened steels at temperatures below the eutectoid transformation.

The present investigation outlines the reaction of these steels to prolonged annealing at temperatures extending from slightly above the eutectoid inversion to above the limit of complete solubility of all the carbon present in the steels. The factors considered relate principally to graphitization, nature and distribution of excess carbides, columnarization of ferrite grains occurring during surface decarburization and fracture grain size of the steels obtained on quenching the annealed specimens.

In contrast to the behavior at subcritical temperatures graphitization above the critical has been shown to correlate with chemical analysis of the steel. Fracture grain size tests in conjunction with metallographic studies have indicated that angular carbides are associated with fine grain size, and that a change in shape to the spheroidal form is accompanied by an increase in fracture grain size. The greater the metallic aluminum content the greater the reluctance of the steels to develop a coarse grain. The tendency for columnarization of the ferrite which occurs during decarburization, has been shown to correlate with grain growth in the adjacent austenite.

THE profound differences in reaction to tempering below the critical range of quenched hypereutectoid steels of similar chemical composition have been discussed by one of the present authors, in

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, Charles R. Austin is professor of metallurgy and M. C. Fetzer is instructor in metallurgy, The Pennsylvania State College, State College, Pa. Manuscript received June 21, 1938.

two recent technical publications.[1] While those researches were not intended to cover a study of dissimilarity to tempering or annealing within the critical range, certain observations were made during the course of the investigation on gradient tempering, which appeared to merit further consideration.

It is the purpose of this paper to present the results of a study of the reaction of five "similar" steels to prolonged annealing at temperatures above the eutectoid inversion and extending to slightly above the Acm or limit of solubility for carbon in iron. The factors considered principally relate to:

1. Relative tendency to graphitization
2. Nature and distribution of excess carbides
3. Fracture grain size of the steels
4. Nature of ferrite grains after surface decarburization

Materials and Experimental Procedure

The steels considered were in the form of ⅜-inch diameter rolled bar stock, and were identical with those previously studied. They are typical of the products of three different steel companies. The chemical analyses of the five steels tested are recorded in Table I.

The research reported on the gradient tempered bars had shown indications that certain of the steels failed to harden properly when quenched after prolonged annealing above the eutectoid temperature and it appeared that surface oxidation and to some extent decarburization were the cause of the irregularities in the hardness data observed. Accordingly a few tests were run to develop suitable technique for minimizing both oxidation and decarburization resulting from either the preheating for quench hardening or from the long annealing treatments which followed.

Satisfactory results were obtained for the hardening treatment by heating in cast iron chips, and by subsequently annealing in high temperature carbon lavite, although in the latter, limited surface decarburization occurred, as will be discussed later.

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[1]Charles R. Austin and B. S. Norris, "Effect of Tempering Quenched Hypereutectoid Steels on the Physical Properties and Microstructures." Transactions, American Society for Metals, Vol. 26, 1938, p. 788.

"Temperature Gradient Studies on Tempering Reactions of Quenched High Carbon Steels," American Institute of Mining and Metallurgical Engineers, *Metals Technology*, June, 1938, pages 1-23. Technical Paper 923.

Eight specimens 1¾ inch long, from each of the five steels were notched ½ inch from one end, held at 1000 degrees Cent. (1830 degrees Fahr.) in cast iron chips for 1 hour and quenched in water. Two of the eight ½-inch notched ends were then broken off from each of the five different steels in order to obtain fracture hardness

Table I

Chemical Analysis of the Steels

Type of Steel	Steel	Carbon	Mn	Si	P	S	Cr	Ni	Va	Cu	Al	Al_2O_3
O. H.	A	1.09/1.09	0.31	0.27	0.018	0.031	0.12	0.06	Nil	0.16	0.005	0.010
E. F.	B	1.04/1.05	0.30	0.44	0.028	0.025	0.05	0.06	Nil	0.12	0.000	0.009
O. H.	D	1.00/1.00	0.42	0.17	0.016	0.027	0.09	0.12	Nil	0.10	0.011	0.008
O. H	E	0.98/0.98	0.40	0.21	0.013	0.031	0.03	0.08	Nil	0.08	0.000	0.009
E. F.	F	1.00/1.00	0.32	0.27	0.009	0.018	0.06	0.16	Nil	0.08	0.025	0.008

data, and to provide specimens for microscopic study. Duplicate specimens of each of the steels were then tempered in carbon lavite salt for 72 hours at 760, at 800, at 840 and at 880 degrees Cent. (1400, 1470, 1545, 1615 degrees Fahr.), followed by water quenching. Again a fracture was taken from one set of specimens from each annealing treatment after this final quench.

Experimental Results

1. *Hardness Data.* After annealing for 1 hour in cast iron chips followed by quenching in water it was noted that all the steels hardened satisfactorily, giving a Rockwell "C" hardness ranging from 62 to 65. Similarly on quenching after tempering or annealing at 760, 800, 840, or 880 degrees Cent. (1400, 1470, 1545, 1615 degrees Fahr.) for 72 hours, all steels fully hardened. The average of several values taken on a cross section of each of the variously treated steels is recorded in Table II.

2. *Fracture Grain Size.* A summary of the observations obtained from a study of the fracture grain size of all the steels after the various heat treatments, followed by water quenching, is assembled in Table III.

The grain size values for the steels quenched from 1000 degrees Cent. (1830 degrees Fahr.) agree with those recorded in the first cited research on these alloys, with the exception of the figure for Steel F which maintained a finer grain than previously. This difference may be due to prehardening treatments X and Y to which the

steels were subjected, in the earlier work, prior to heating and quenching from 1000 degrees Cent. (1830 degrees Fahr.). A general picture of the relation between fracture grain size and annealing temperature (72 hours duration) is shown diagrammatically (Fig. 1).

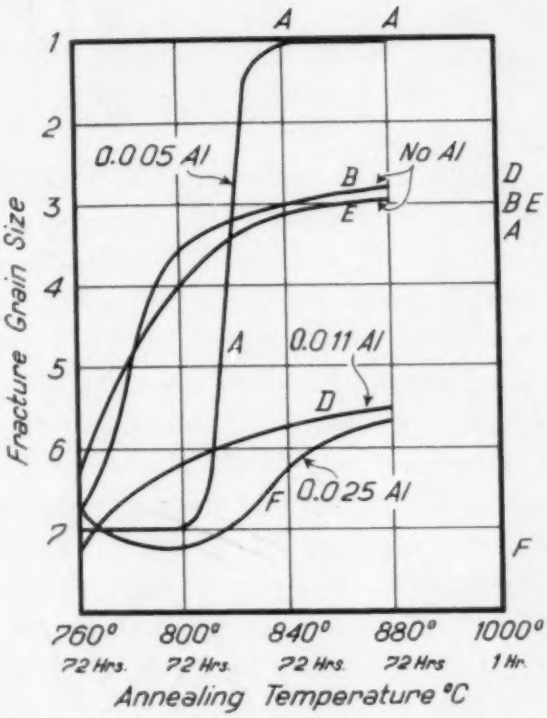


Fig. 1—Relation Between Fracture Grain Size and Temperature of Annealing Prior to Quenching, for Each of the Five Steels Investigated.

All steels were fine-grained after 72 hours at 760 degrees Cent. (1400 degrees Fahr.), three steels maintained their fine grain character at 800 degrees Cent. (1470 degrees Fahr.), but only two, steels D and F, were still fine-grained after 72 hours at 840 and 880 degrees Cent. (1545 and 1615 degrees Fahr.). The reluctance of the steels to coarsen as the annealing temperature increased, appeared to correlate with their metallic aluminum content.

3. *Microstructural Characteristics.* The profound differences observed in tendency to graphitization of these steels, at temperatures below the critical, have been recorded.[2] Dissimilarity in the nature and distribution of the spheroidal cementite on prolonged tempering at sub-critical temperatures has also been discussed and illustrated[3].

[2]loc cit.
[3]loc cit.

The behavior of the steels with respect to these characteristics, as well as to surface decarburization, at temperatures within the critical range, is now to be outlined under the sub-headings graphitization, spheroidized free cementite, and surface decarburization.

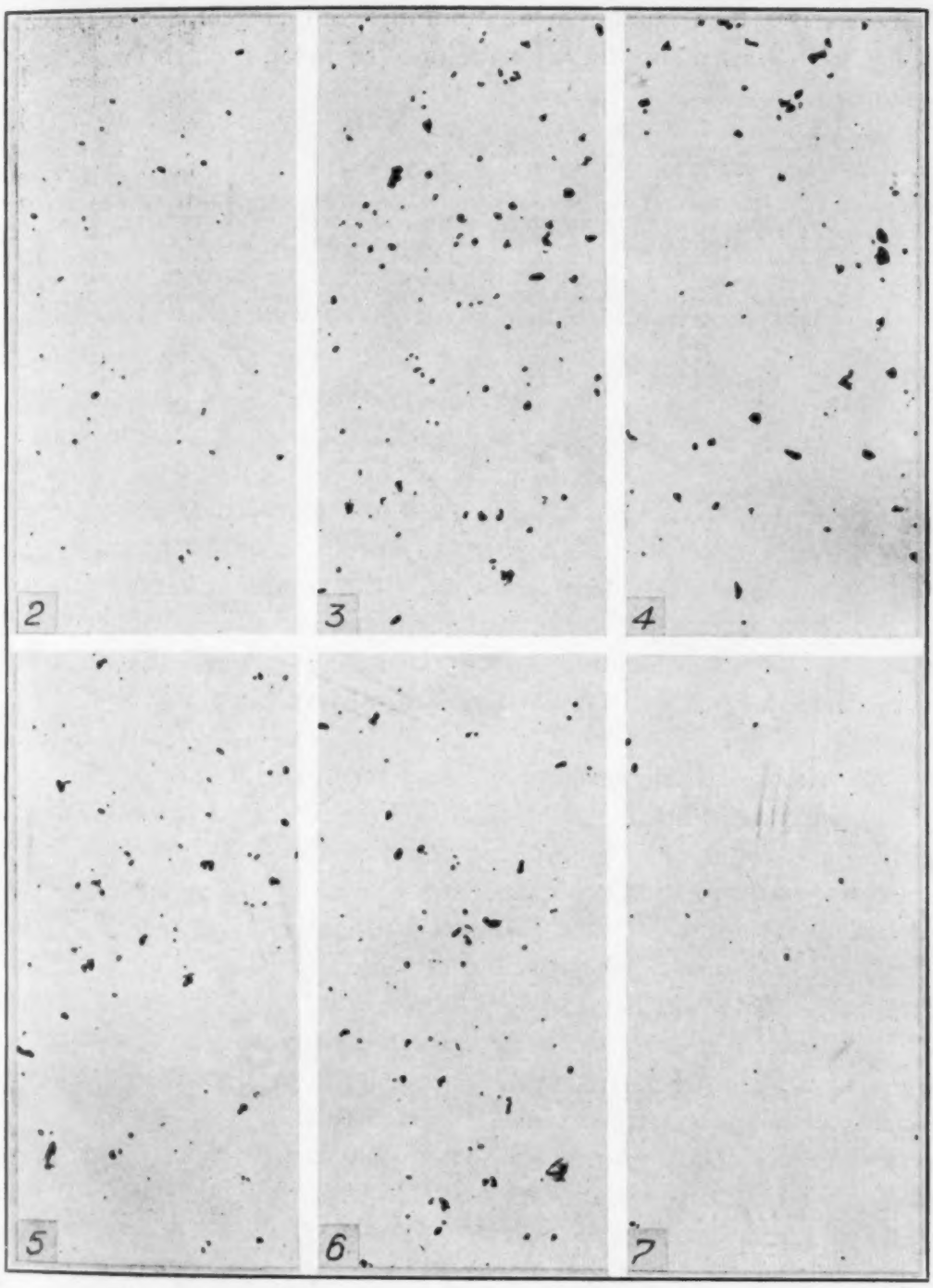
A. *Graphitization.* After annealing for 72 hours at 760, 800, 840 and 880 degrees Cent. (1400, 1470, 1545, 1615 degrees Fahr.), and water quenching, samples for microscopic examination were ground and polished and typical structures recorded, as in Figs. 2 to 10 inclusive, at 100 diameters.

At 760 degrees Cent. (1400 degrees Fahr.) steel A exhibited a slight tendency to graphite formation (Fig. 2), whereas at 800 and 840 degrees Cent. (1470 and 1545 degrees Fahr.) (Figs. 3 and 4) marked graphitization occurred. Steel B graphitized readily at each of the three lower annealing temperatures (Figs. 5 and 6). Very little graphitization was observed in steel D (Fig. 7) or steel E at any of the four temperatures. Steel F exhibited marked graphitization at 760 and 800 degrees Cent. (1400 and 1470 degrees Fahr.) (Figs. 8 and 9) but was practically free from graphite after annealing for 72 hours at 840 degrees Cent. (1545 degrees Fahr.) (Fig. 10). All steels were practically free from any graphitization as a result of the 880 degrees Cent. (1615 degrees Fahr.) anneal. The graphitizing characteristics of these steels as a function of annealing temperature is depicted in Fig. 11.

At subcritical temperature steels A, D, and F graphitized while steels B, C, and E were very resistant to graphitization. No evidence of graphitization was found in any of the steels after the preliminary 1 hour at 1000 degrees Cent. (1830 degrees Fahr.).

B. *Spheroidized Free Cementite.* Subsequent to the studies on graphitization the specimens were etched in order to reveal the nature and distribution of the free cementite. A few typical structures obtained on etching in 1 per cent nitric acid in absolute ethyl alcohol are recorded in Figs. 12 to 18.

The excess carbides after 72 hours at 760 degrees Cent. for steels B and F are shown in Figs. 12 and 13 respectively at 1000 diameters. These structures are typical of all five steels, and it will be observed that there are two distinct groups of carbides (a) very small spheroidal ones and (b) large angular carbides. Upon increasing the annealing temperature to 800 degrees Cent. the small particles disappear. The large carbides then had a spheroidal form in steels B and E. (Fig. 14) but were still angular in steels A, D, and F



Figs. 2 to 7—Photomicrographs Showing the Amount of Graphite Formed in Various Steels on Quenching After 1 Hour at 1000 Degrees Cent. Followed by 72 Hours Annealing at the Temperature Indicated. Unetched. × 100.

Steel A. Fig. 2, at 760° C.; Fig. 3, at 800° C.; Fig. 4, at 840° C. Steel B. Fig. 5, at 760° C.; Fig. 6, at 800° C. Steel D. Fig. 7, at 800° C.

(Figs. 15, 16, and 17). It may be noted that steels B and E contain the least amount of carbide-forming element, chromium; they are the

only steels which contain no aluminum; and at 800 degrees Cent. it has been shown that they are the only two steels which are coarse-grained.

Table II

Rockwell "C" Hardness of the Steels After Water Quenching From 1 Hour at 1000 Degrees Cent. and After Subsequently Annealing for 72 Hours at 760, 800, 840 and 880 Degrees Cent. Followed By Requenching in Water

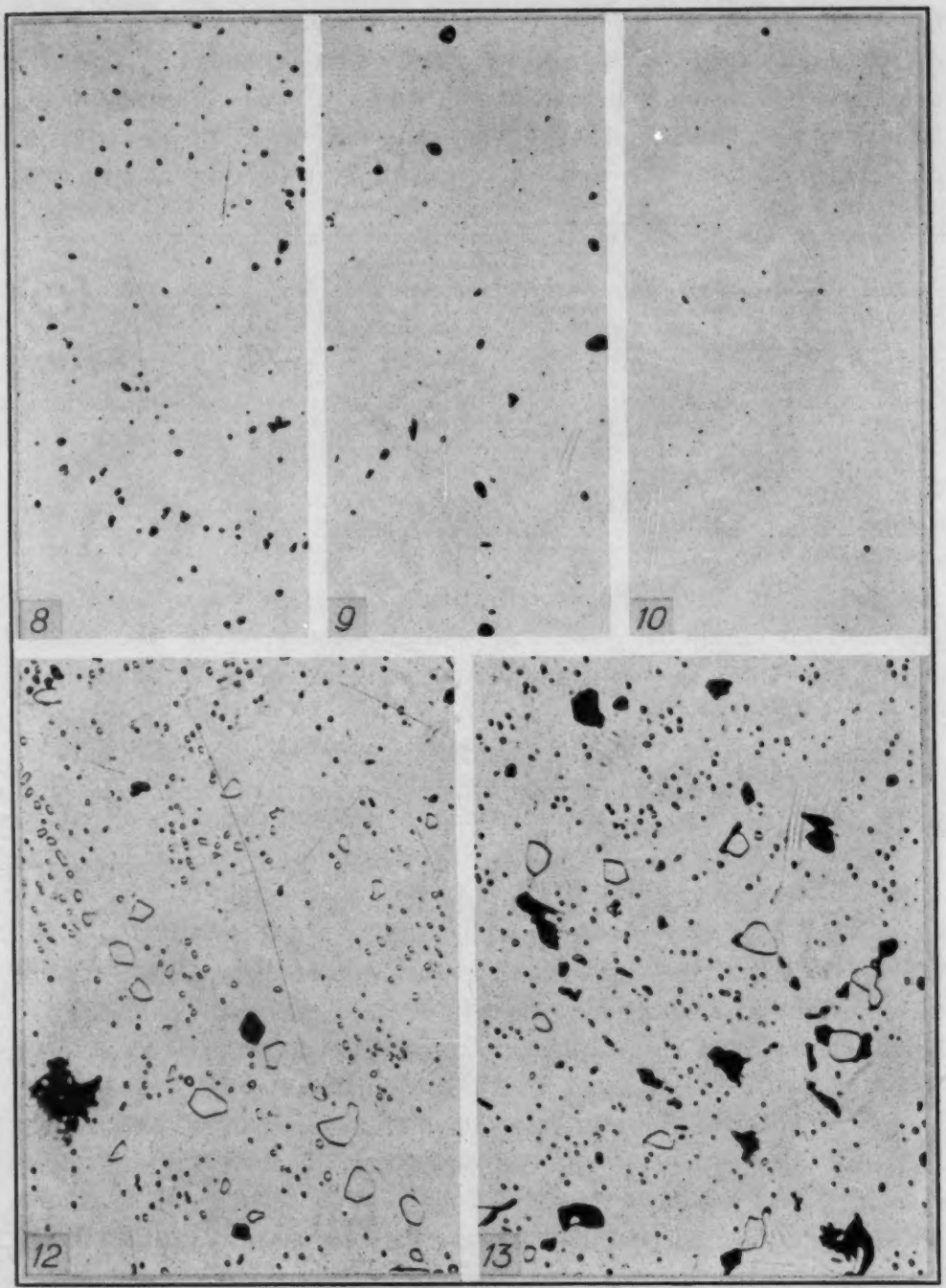
Steel	1 Hour at 1000°C and Water Quench	1000°C—W.Q. 760°—72 Hour Water Quench	1000°C—W.Q. 800°C—72 Hour Water Quench	1000°C—W.Q. 840°C—72 Hour Water Quench	1000°C—W.Q. 880°C—72 Hour Water Quench
A	64.0	65.3	64.0	62.9	64.9
B	65.2	64.7	63.5	63.1	64.8
D	63.6	63.0	62.3	63.9	64.0
E	63.0	64.1	62.8	63.8	64.0
F	64.4	63.5	63.1	63.5	64.9

At 840 degrees Cent. all the carbides appeared to have passed into solution (except steel A, Fig. 18) or to have decomposed with the formation of graphite. Incidentally the residual carbides in steel A showed a change to the rounded form and the steel became coarse-grained. Complete solution of all the carbon present in the steels was effected, apparently, by the prolonged treatment at 880 degrees Cent.

C. *Surface Decarburization.* As a result of the initial treatment for all specimens, heating 1 hour at 1000 degrees Cent. (1830 degrees Fahr.) and water quenching, being conducted in cast iron chips, little surface decarburization occurred. Subsequent annealing for 72 hours in carbon lavite at 760, 800, 840 and 880 degrees Cent. (1400, 1470, 1545, 1615 degrees Fahr.) resulted in some decarburization in all the steels at each temperature.

The polished cross sections of treated specimens were etched in 1 per cent alcoholic nitric acid. This reagent produced a light martensitic etch and clearly revealed the structure of any free carbides. Near the peripheral part of the sample a darker etching ring was observed adjacent to the outer zone of ferrite. This peripheral zone of ferrite was absent in the samples annealed for 72 hours at 880 degrees Cent. (1615 degrees Fahr.). In the intermediate ring where a concentration gradient existed due to partial decarburization, there was an absence of free carbides or graphite. A synopsis of the observations made on the depth and nature of surface decarburization has been assembled in Table IV.

Of particular interest is the type of grain developed in the ferrite at the various annealing temperatures. Several writers have



Figs. 8 to 13—Microsections on Quenching After 1 Hour at 1000 Degrees Cent. Followed by 72 Hours Annealing at the Temperature Indicated.

Figs. 8 to 10—Unetched Sections Showing Amount of Graphitization. × 100.
Steel F. Fig. 8, at 760° C.; Fig. 9, at 800° C.; Fig. 10, at 840° C.

Figs. 12 and 13—Etched Sections Showing Free Cementite and Some Transformed Pearlite (Fig. 13). Etched Nital. × 1000.
Steel B. Fig. 12, at 760° C. Steel F. Fig. 13, at 760° C.

discussed the mode of formation of columnar grains in the decarburized zone of a steel, and the theory first proposed by Green in a discussion of a paper by one of the present authors[4] appears to find most favor. This theory suggests that nuclei of the new ferritic phase formed from the austenite, by elimination of the carbon from

Table III

Fracture Grain Size of the Steels After Water Quenching From 1 Hour at 1000 Degrees Cent., and After Subsequently Annealing for 72 Hours at 760, 800, 840 and 880 Degrees Cent. Followed By Requenching in Water

Steel	1 Hour at 1000°C and Water Quench	1000°C—W.Q. 760°C—72 Hour Water Quench	1000°C—W.Q. 800°C—72 Hour Water Quench	1000°C—W.Q. 840°C—72 Hour Water Quench	1000°C—W.Q. 880°C—72 Hour Water Quench
A	3¼	7	7	1	1
B	3	6¾	3½	3	2¾
D	2¾	7¼	6¼	5¾	5½
E	3	6¼	4	3	3
F	7¼	6¾	7¼	6¼	5½

the surface of the steel, grow inward progressively as decarburization and concomitant γ-α phase change occurs. The mechanism can be compared to that of columnar growth during freezing from the liquid state.

Mehl[5] considers this explanation incontestable, although he points out that columnar crystals may develop from the solid state in other ways.[6]

Discussion of Results

In order to correlate the effect of prolonged annealing on the various steels after quenching from 1000 degrees Cent. (1830 degrees Fahr.), a series of diagrammatic sketches were prepared to indicate qualitatively the progress of graphitization, the nature and distribution of the spheroidized cementite, the amount of surface decarburization, and the form, columnar or equiaxed, of the resulting ferrite grains. These data are presented in Fig. 21.

It is now proposed to discuss more fully some of the important characteristic differences observed in the series of steels.

Hardness and Critical Cooling Rates. The present study indi-

[4]G. W. Green—discussion of paper by Charles R. Austin, "Hydrogen Decarburization of Carbon Steels with Considerations on Related Phenomena." Journal of The Iron and Steel Institute, Vol. CV, No. I, 1922, pages 93-155.

[5]R. F. Mehl, "Diffusion in Solid Metals," Inst. of Metals Div., Lecture, American Institute Mining and Metallurgical Engineers, Vol. 122, 1936, p. 11-56.

[6]D. H. Rowland and Clair Upthegrove, "Grain Size and Its Influence on Surface Decarburization of Steels," Transactions, American Society for Metals, Vol. XXIV, March 1936, p. 96-132.

cates conclusively that all the steels completely harden when water quenched from above the lower critical point. The irregularities previously recorded were, as suspected, largely due to the effects of surface oxidation, resulting from prolonged annealing in air prior to quenching.

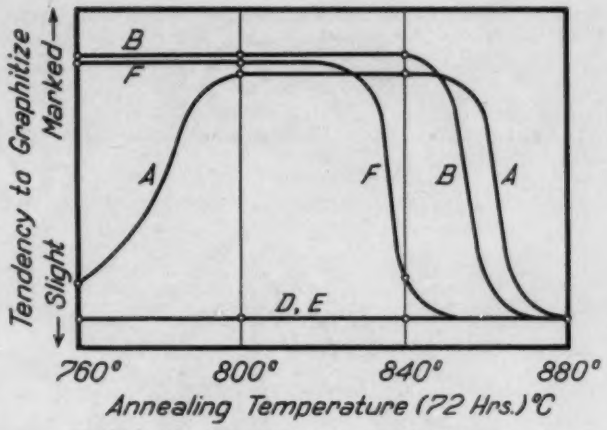


Fig. 11—Graphitizing Tendencies of the Five Steels as a Function of Annealing Temperature.

It is of importance in this connection to consider also the relative critical cooling rates of the steels as indicated by the microstructures obtained on quenching the annealed steels when free from scale. Thus Fig. 13, which illustrates the microstructure of steel F, water-quenched after annealing 72 hours at 760 degrees Cent. (1400 degrees Fahr.), shows evidence of small regions of pearlite—the black areas in this section must not be mistaken for graphite. Since the cooling rate obtained on quenching from 760 degrees Cent. (1400 degrees Fahr.) evidently approximated the critical cooling velocity, any appreciable scaling would have prevented complete hardening of this fine-grained steel.

Steels A, D, and E, fine-grained at 760 degrees Cent. (1400 degrees Fahr.), also showed some evidence at high magnification of scattered regions of transformed pearlite, when quenched from this temperature.

On quenching from 800 degrees Cent. (1470 degrees Fahr.) steel F showed traces of fine pearlite, but none could be observed in any of the other four steels similarly treated.

A further indication of the relative reactivity of the steels is provided by the amount of fine pearlite observed in the martensite adjacent to the ferrite formed in the decarburized peripheral ring.

Thus, on quenching from 760 degrees Cent. (1400 degrees Fahr.) steel F showed as much as 50 per cent fine pearlite in the transition zone while steel B showed none. Steels A, D, and E had intermediate

Table IV

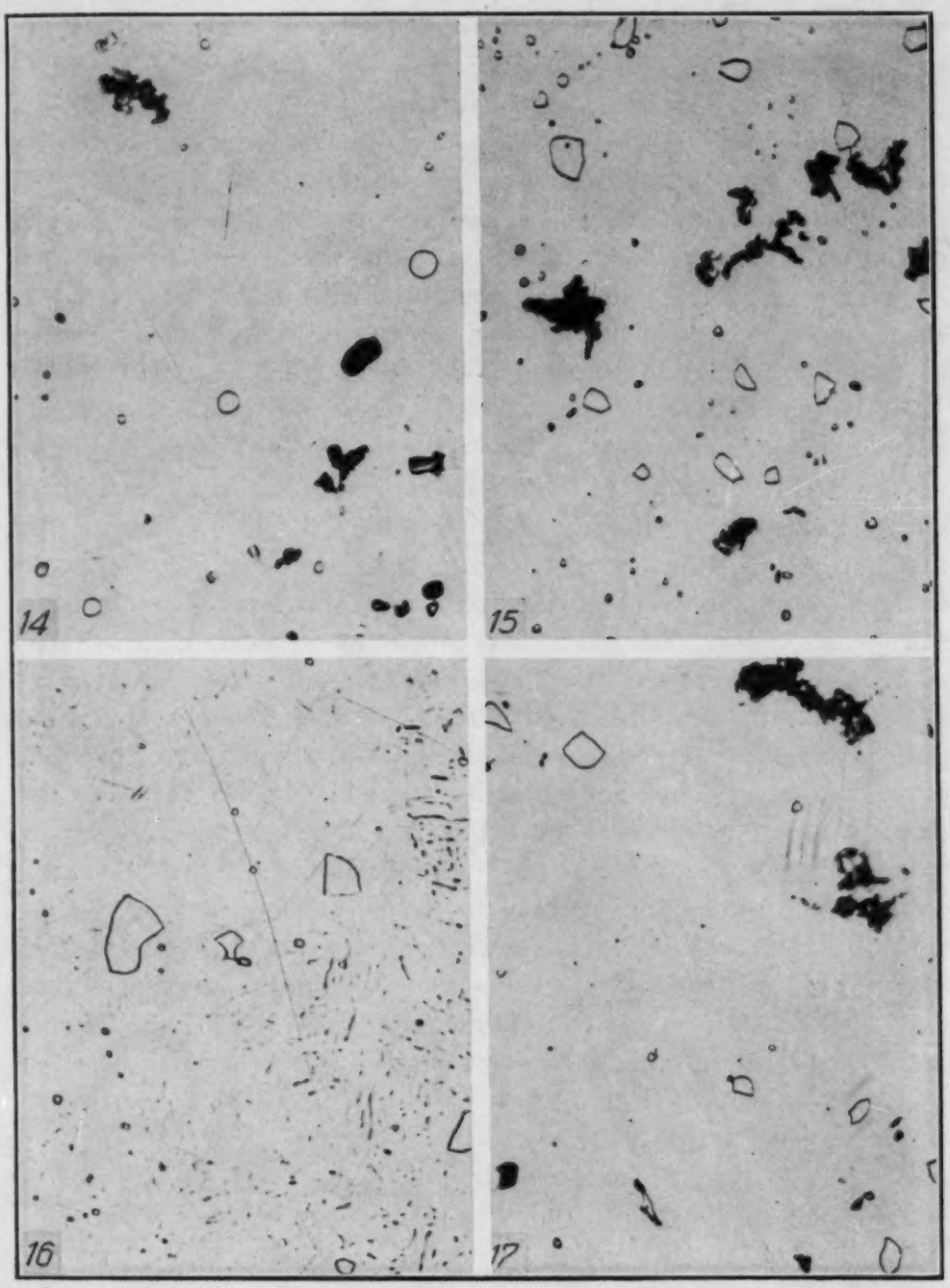
Synopsis of Observations Taken on Depth and Nature of Surface Decarburization of the Steels During 72 Hours Anneal at 760, 800, 840 and 880 Degrees Cent.

Steel	Annealed 72 hours at Degrees Cent.	Decarburized Band of Ferrite Depth m.m.	Decarburized Band of Ferrite Grain Type	Gamma Grain Size Adjacent to Ferrite By Microscope	Gamma Grain Size Adjacent to Ferrite By Fracture	Nature of Ferrite-Martensite Boundary
A	760	0.75	Equiaxed	7-8	As F.G.S.*—7	Irreg. Mixed α -M
B	760	1.0	Columnar	..	Coarser than 6¾†	Sharp. Fig. 19
D	760	0.75	Equiaxed	7	As F.G.S.—7¼	Irreg. Mixed α -M
E	760	0.8	Columnar	3-4	Coarser than 6¼	Sharp
F	760	0.75	Equiaxed	7-8	As F.G.S.—6¾	Irreg. Fig. 20
A	800	0.5	Columnar	3-4	Coarser than 7	Irreg. No mixed α -M
B	800	0.75	Columnar	Approx. 4	As F.G.S.—3½	Irreg. No mixed α -M
D	800	0.4	Equiaxed	7	As F.G.S.—6¼	Irreg. Mixed α -M
E	800	0.6	Columnar	4-5	As F.G.S.—4	Irreg. No mixed α -M
F	800	0.5	Mixed	Mixed	As F.G.S.—7¼	Irreg. Mixed α -M
A	840	0.2	Columnar	..	Stony—1	Sharp
B	840	0.6	Columnar	Approx. 3-4	As F.G.S.—3	Sharp
D	840	0.35	Mixed	..	As F.G.S.—5¾	Irreg. Mixed α -M
E	840	0.4	Columnar	Approx. 4	As F.G.S.—3	Sharp
F	840	0.35	Mixed	Mixed	As F.G.S.—6¼	Irreg. Mixed α -M‡
A to F	880	None	..	..	..	

*Fracture Grain Size.
†Fracture Grain Size recorded in Table III.
‡In this steel a few large austenite (martensite) grains are associated with ferrite columnarization and a sharply defined boundary (cf. Fig. 20).

amounts. After quenching from 800 degrees Cent. (1470 degrees Fahr.) two steels, B and E, showed no evidence of pearlite, whereas quenching from 840 degrees Cent. (1545 degrees Fahr.) steels B, E, and A were completely martensitic. Hence steels A, D, and F at 800 and steels D and F at 840 degrees Cent. (1470, 1545 degrees Fahr.) all exhibited evidence of the presence of some pearlite network in the intermediate zone, thus indicating the greater difficulty in suppressing the eutectoid inversion in the given steels under the quenching conditions cited. A comparison of this reactivity with grain size, shows a satisfactory correlation. The fine-grain steels exhibit a greater tendency to formation of fine pearlite.

These facts readily explain why certain steels in the previous work on gradient tempering failed to harden when the quenching rate



Figs. 14 to 17—Photomicrographs Showing the Amount, Nature and Distribution of Free Cementite of Steels Annealed 72 Hours at 800 Degrees Cent. and Water-Quenched. Light Etching in Nital Does Not Reveal the Martensitic Matrix. × 1000.

Fig. 14, Steel B. Fig. 15, Steel A. Fig. 16, Steel D. Fig. 17, Steel F.

was appreciably slowed down by the presence of scale on the specimens.

Tendency to Formation of Graphite. In previously published researches by one of the present authors[7] it has been shown that the tendency toward graphitization at sub-eutectoid temperatures could not be related to the amount of elements usually considered as promoting or inhibiting this phenomenon. This can readily be confirmed by referring to Table I, containing the chemical analysis of the steels, when it is recalled that steels B and E showed little tendency to graphite formation between 600 and 700 degrees Cent. (1110, 1290 degrees Fahr.), whereas steels A, D, and F graphitized freely.

On prolonged annealing above the lower critical the grouping of the steels is quite different as evidenced by the graphitizing tendency chart given in Fig. 11. Thus steel B which exhibited particularly strong resistance to formation of graphite at 650 degrees Cent. (1200 degrees Fahr.), graphitized strongly and to about the same extent at each of the three lower temperatures studied, 760. 800, and 840 degrees Cent. (1400, 1470, 1545 degrees Fahr) (Figs. 5 and 6). On the other hand, steel E showed strong resistance to graphitization whether annealed below or above the eutectoid temperature. Steel D while graphitizing freely at 650 degrees Cent. (1200 degrees Fahr.) showed little graphite when annealed at 760 to 840 degrees Cent. (1400-1545 degrees Fahr). Steels A and F both graphitized freely at two of the three temperatures studied within the critical range. The exceptions noted were at 760 degrees Cent. (1400 degrees Fahr.) in the case of A, and in the 840 degrees Cent. (1545 degrees Fahr.) treatment for F. Thus on the basis of graphitization the steels can be placed in two groups:

	Sub-eutectoid Temperature	Temperatures Within the Critical Range
Prone to graphitization	A, D, and F	A,* B, and F*
Resistant to graphitization	B and E	D and E

In considering annealing temperatures above the lower critical it appears possible to correlate carbide instability with the chemical analysis of the steels. For the steels which graphitize, the silicon content is highest, 0.44, 0.27 and 0.27 per cent for B, A, and F as compared with 0.17 and 0.21 per cent for steels D and E. Again

[7] loc cit.

*Steels A and F were resistant at 760 and 840 degrees Cent. (1400 and 1545 degrees Fahr.) respectively.

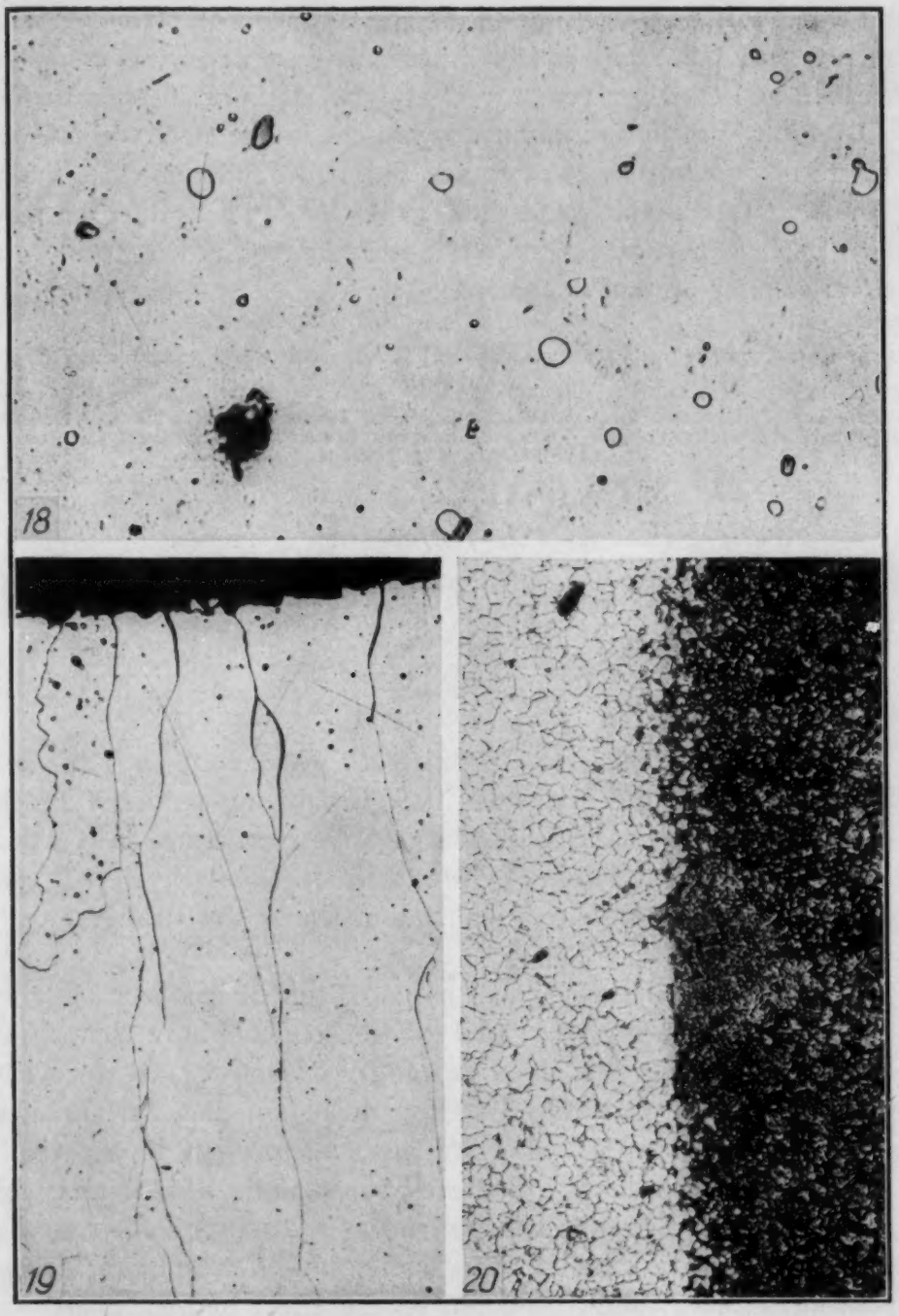


Fig. 18—Photomicrograph of Steel A, the Only Sample Showing Free Cementite After Quenching Following 72 Hours Anneal at 840 Degrees Cent. Etched in Nital. × 1000.

Figs. 19 and 20—Steels B and F Respectively Annealed 72 Hours at 760 Degrees Cent. and Water-Quenched. Etched in Nital. × 100. The Dark Areas are Martensite and the Sections Illustrate the Nature of the α-γ Boundary and the Ferrite Grains.

for the graphitizing steels B, A, and F, the carbide stabilizer manganese is only 0.30, 0.31 and 0.32 per cent respectively, as compared with 0.42 and 0.40 per cent for D and E. It is of interest to note the algebraic sum of the impurities present in the steel with respect to their known tendency to promote (Si, Ni, Al and Cu) or to inhibit (Cr and Mn) graphitization (see Table V). The value for manganese used, is that in excess of the amount required to form MnS with all sulphur present in the steel.

Table V

Computation of Algebraic Sum of Weight Per Cent Elements Present Which Promote Graphitization (Positive) and Which Stabilize the Cementite (Negative), for Each of the Five Steels Investigated.

	Graphitizers								Stabilizers				
Steel	Per Cent Si		Per Cent Ni		Per Cent Cu		Per Cent Al		Per Cent Mn over MnS		Per Cent Cr		Total
A	0.27	+	0.06	+	0.16	+	0.005	−	0.26	−	0.12	=	+0.115
B	0.44	+	0.06	+	0.12	+	0.000	−	0.26	−	0.05	=	+0.31
D	0.17	+	0.12	+	0.10	+	0.011	−	0.37	−	0.09	=	−0.06
E	0.21	+	0.08	+	0.08	+	0.000	−	0.35	−	0.03	=	−0.01
F	0.27	+	0.16	+	0.08	+	0.025	−	0.29	−	0.06	=	+0.185

Whether fortuitously or otherwise, the greater the algebraic sum of these quantities the greater is the graphitizing tendency of the steels. Thus steels D and E with a negative summation are particularly resistant to dissociation of the cementite. Similarly steel B with the highest value for positive summation shows the strongest tendency to graphitize.

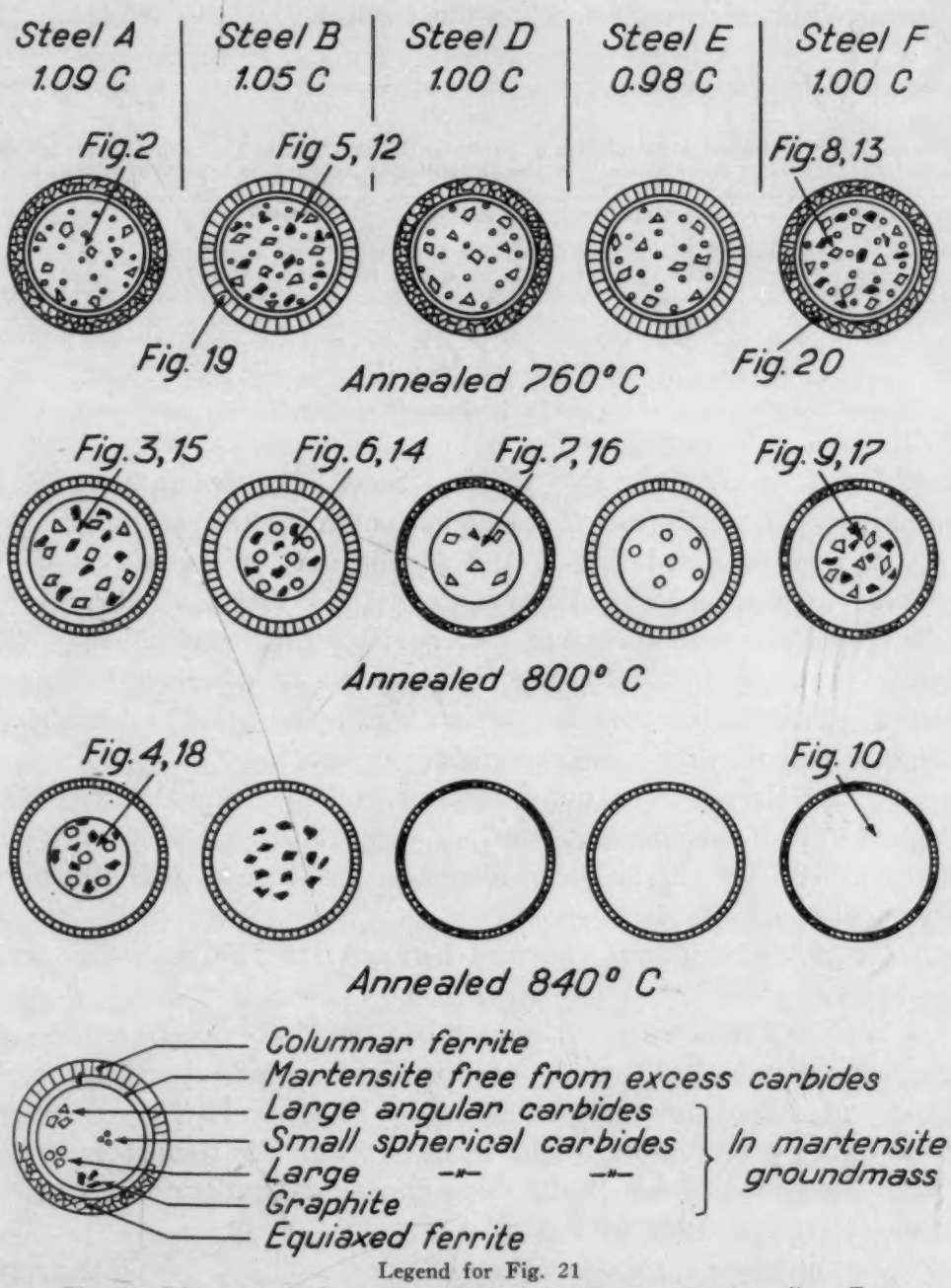
In these computations it will be noted that it has been assumed that equal weights per cent of each of the elements have comparable effects on production or inhibition of graphitization. A review of the literature[8] was made in an attempt to obtain data pertaining to the relative effects of the chemical elements present in the steels. From various data relating principally to graphitization of malleable cast iron a relative graphitizing potency (positive or negative) has been deduced for chromium, manganese, nickel, aluminum, copper and silicon. Since the information on the effect of manganese was too uncertain, it has been assumed to be equal but opposite in effect

[8] J. L. Gregg and B. N. Daniloff, "Alloys of Iron and Copper Monograph," page 273.
F. L. Coonan, "Alloying Elements in Malleable Iron," *Foundry*, Oct. 1933, page 43.
H. A. Schwartz, "Graphitization in the Presence of Nickel," TRANSACTIONS, American Society for Steel Treating, Vol. XV, 1929, p. 957-70.
H. A. Schwartz, H. H. Johnson, and C. H. Junge, "Retarding Effects of Certain Metallic Elements on Graphitization," TRANSACTIONS, American Society for Metals, Vol. XXV, 1937, p. 609-36.
M. F. Renaud, *Revue de Metallurgy Memoirs*, 1933, p. 256.

to silicon. The following expression shows the relationship.

$$-\text{Cr} = -3/2\ \text{Mn} = +3\ \text{Ni} = +2/3\ \text{Al} = +5\ \text{Cu} = +3/2\ \text{Si}$$

Using these relative factors for graphitizing or inhibiting power,



Legend for Fig. 21

Fig. 21—Diagrammatic Synopsis of the Relation Between the Annealings Temperatures of 760, 800 and 840 Degrees Cent. and

(1) Amount, Shape and Size of Free Cementite
(2) Graphitizing Tendency of the Steels
(3) Extent of the Effect of Partial Decarburization
(4) Nature of Ferrite Grains in Peripheral Decarburized Zone.

and basing the computations on chemical analysis as was done in Table V the following values result (Table VI).

The same general correlation is obtained with the steels having the greatest tendency toward graphitization (B and F) showing positive algebraic summations, while those which lack this tendency (D and E) have high negative values. Steel A, although showing a negative value graphitizes at the higher annealing temperatures.

Table VI

Computation of Probable Graphitizing Tendency of the Steels, Using a Factor for the Relative Effects of the Elements in the Graphitizing or Carbide Stabilizing Tendencies.

	Graphitizers										Stabilizers				
Steel	Per Cent Si x ⅔		Per Cent Ni x ⅓		Per Cent Cu x ⅓		Per Cent Al x 3/2		Per Cent Mn x ⅔ over MnS		Per Cent Cr x 1		Total
A	0.18	+	0.02	+	0.03	+	0.008	−	0.17	−	0.12	=	−0.05
B	0.29	+	0.02	+	0.024	+	0.000	−	0.17	−	0.05	=	+0.115
D	0.10	+	0.04	+	0.02	+	0.016	−	0.25	−	0.09	=	−0.165
E	0.14	+	0.03	+	0.016	+	0.000	−	0.23	−	0.03	=	−0.075
F	0.18	+	0.05	+	0.016	+	0.038	−	0.19	−	0.06	=	+0.035

It may be noted that B and A, the only two steels showing graphite formation at 840 degrees Cent. (1545 degrees Fahr.), contain the highest carbon content. Presumably this temperature is still below the Acm (or Agr) line for these steels, whereas the upper critical has been exceeded for steels D, E, and F, this fact bringing the last steel into the non-graphitizing group.

It has already been noted that on prolonged annealing at 880 degrees Cent. (1615 degrees Fahr.), a temperature which is above the upper critical for all steels considered, no evidence of graphitization was obtained.

No relationship was observed between fracture grain size and tendency to graphitize.

Carbide Coalescence. Attention has already been directed to the angular or spherical nature of the free carbide particles, and typical microstructure are furnished in Figs. 12 to 18. A more readily correlated picture of the form in which the cementite develops in the various steels at the three annealing temperatures, can be obtained from a study of Fig. 21.

On annealing for 72 hours at 760 degrees Cent. (1400 degrees Fahr.) all steels contain groups of very small rounded carbides as well as large angular ones (see Fig. 12). All these steels are fine-grained. Upon increasing the annealing temperature to 800 degrees

Cent. (1470 degrees Fahr.), all small spheroidal carbides were apparently taken into solution, and the angular carbides in steels B and E assumed the circular form (Fig. 14). Both these steels coarsened to fracture grain size 3-4 during the 72 hour treatment. In steels A, D, and F the angular form of the carbides persisted, and all three steels maintained their fine-grained characteristics.

At 840 degrees Cent. (1545 degrees Fahr.) free carbide persisted only in steel A (1.09 per cent carbon) but the particles assumed a spheroidal form and the steel coarsened during treatment. Despite the apparent complete solution of the free cementite in D and F, these steels did not coarsen appreciably. This fact was equally true after annealing at 880 degrees Cent. (1615 degrees Fahr.). However, the steels are both high in metallic aluminum content.

Decarburization and Resulting Ferrite Characteristics. No appreciable decarburization occurred during the initial treatment for 1 hour at 1000 degrees Cent. (1830 degrees Fahr.), but all steels showed some surface loss of carbon during all subsequent annealing treatments. There were noted the usual zones of decarburization, one of ferrite, a second or diffusion concentration gradient of martensite where all carbon had been taken into solution prior to quenching, and a third zone containing free excess carbides in a martensitic matrix which represented the true structure of the steel having the original carbon analysis. The lower the temperature of anneal the more abrupt was the change from the first to the third zone, and the greater the width of the pure ferrite peripheral band.

While the amount of decarburization was naturally of the same order of magnitude in all steels, the difference in the width of the band of ferrite was sufficient to examine quantitatively. Fig. 22 indicates that the steels (B and E) which were free from metallic aluminum, and had the coarsest austenitic grain size, exhibited the most decarburization in terms of free ferrite.

The thinner ferrite band obtained with increase in annealing temperature is attributed to increase in rate of carbon diffusion. The absence of any ferrite band at 880 degrees Cent. (1615 degrees Fahr.) may not wholly be accounted for by increase in rate of diffusion of carbon. It is probable that the carbon lavite salt used in these experiments is actually less prone to produce decarburization at the higher annealing temperatures.

The most interesting feature of this phase of the investigation relates to the shape, equiaxed or columnar, of the peripheral ferrite.

The reaction of ferrite to surface decarburization in this respect is summarized in Fig. 21 for all five steels at each of the three annealing temperatures.

According to the nucleating theory advanced by Green,[9] steels

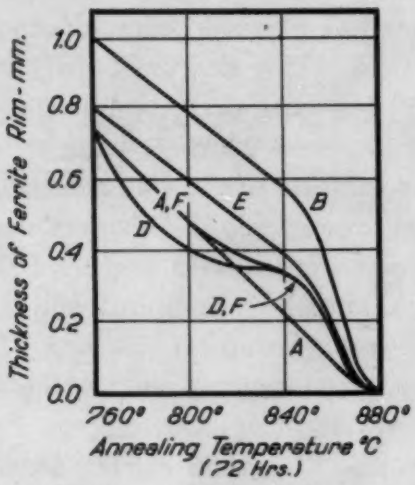


Fig. 22—Relation Between Thickness of Surface Decarburized Ferrite Zone and Annealing Temperature for Each of the Five Steels Investigated.

decarburized within the critical range should exhibit columnar development of the surface grains as the gamma-alpha inversion occurs, at constant temperature, by virtue of the loss of carbon.

Since no ferrite band was found after annealing at 880 degrees Cent. (1615 degrees Fahr.) the following comments refer only to those temperatures of anneal, 760, 800, and 840 degrees Cent. (1400, 1470, 1545 degrees Fahr.), which approximate the temperature interval between the lower and upper critical points.

Only two steels, B and E, show columnarization at 760 degrees Cent. (1400 degrees Fahr.), and these two steels develop columnar ferrite at each of the three temperatures studied. Steels A, D, and F exhibit quite definitely a truly equiaxed ferrite grain on treating at this lowest temperature, and the characteristic persists in steel D after surface decarburization at 800 degrees Cent. (1470 degrees Fahr.). At this intermediate temperature the other four steels are at least partially columnar, but while steels A, B, and E are wholly columnar, a preponderance of equiaxed ferrite grains is found in steel F—designated as "mixed" in Table IV.

[9] loc cit.

At 840 degrees Cent. (1545 degrees Fahr.) steels A, B, and E are again entirely columnar, and steels D and F, while designated as mixed, exhibit a greater proportion of equiaxed carbon free ferrite. Thus the tendency toward columnarization of the free ferrite increases as the temperature of anneal, within the critical range, is increased. This observation does not correlate with the nucleating theory of Green, and evidently some other factor has a controlling influence. The data indicate a relation between ferrite form and the size of the austenitic grain from which the ferrite develops isothermally.

Steels B and E are typical coarse-grain steels having a low coarsening temperature, and both steels exhibit strong ferrite columnarization at each of the annealing temperatures. Steels D and F have fine-grained characteristics and are least prone to lose the normal equiaxed form of the ferritic grains. Steel A is intermediate in its reaction to austenitic grain growth on annealing, and forms equiaxed ferrite grains at 760 degrees Cent. (1400 degrees Fahr.) and columnar ferrite at the higher temperatures.

Thus austenitic grain size appears to have a definite influence on the shape of the ferrite grains which develop at constant temperature, within the critical range during surface decarburization. When the gamma grain is large, columnar ferrite is produced, and when the gamma grain is small, equiaxed ferrite may be anticipated.

Two photomicrographs have been included to illustrate this feature. Fig. 19 shows a section of steel B after annealing at 760 degrees Cent. (1400 degrees Fahr.). The austenitic grain size is shown as 6¾, but the gamma size adjacent to the ferrite, while difficult to approximate under the microscope, appeared very similar to that of steel E, which was clearly defined at 3-4 (Table IV). In the microsection, the tempered martensite was etched black in order to permit clear etching of the ferrite grains. Tempering of the martensite occurred during mounting of the specimen to facilitate polishing.

Fig. 20 illustrates the equiaxed ferrite obtained in a fine-grain steel decarburized at 760 degrees Cent. (1400 degrees Fahr.). In this section it is clearly shown that the size of the gamma grain (dark martensite) was comparable to the small size of equiaxed ferrite grain resulting from decarburization. In the center of the picture may be noted a single coarse austenitic grain. Adjacent to this transformed crystal, tendency to columnarization is apparent.

Thus in general a coarse-grained steel forms columnar grains

and a fine-grain steel forms equiaxed grains of ferrite on decarburization. However, when austenitic grain growth occurs in the transition zone, between the peripheral ferrite band and the unaltered core (Table IV), the grain size of this transition zone is the controlling factor with regard to the type of ferrite grain developed.

The nature of the boundary adjacent to the ferrite band merits a comment. When the intermediate martensite zone was fine-grained and adjacent to equiaxed ferrite, the alpha-martensite boundary was irregular and consisted of a mixture of fine-grained ferrite and martensite. This characteristic is shown in Fig. 20.

Green[10] has drawn attention to the suggestion that duplexity, meaning the presence of both ferrite and austenite in localized areas, results in obstruction to grain growth, and hence in the development of small equiaxed grains.

When the intermediate zone was coarse-grained a fine clearly defined boundary existed next to the columnar ferrite, as shown in Fig. 19.

The tendency for columnarization from the coarse martensite grain in steel F at 760 degrees Cent. (1400 degrees Fahr.) (center of Fig. 20) has already been mentioned. It is of interest to note the sharp nature of the boundary in this localized area, as well as the freedom from interpenetration of the austenite (martensite)—ferrite phases.

Conclusions

1. All the steels fully hardened when water-quenched from 760, 800, and 840 degrees Cent. (1400, 1470, 1545 degrees Fahr.) after annealing for 72 hours. However, the quenching rate in some steels approximated very closely to the critical cooling rate even when the steels were free from scale. The reason for imperfect hardening under similar heat treatment noted in the earlier work on gradient tempering was evidently due to the presence of scale on the surface of the steels.

2. The factors controlling graphitization above the euctectoid inversion are different from those obtaining at sub-critical temperatures. Graphitization within the critical range has been shown to correlate with the relative amounts present of known graphitizing

[10] loc cit.

elements (Si, Ni, Al and Cu) and carbide stabilizers (Mn and Cr).

3. A relationship has been shown between fracture grain size and shape of the massive carbide particles. Angular carbides are associated with fine-grained steels and equiaxed or spheroidal carbides with coarse-grained steels. However, it is probable that the same factor which controls austenitic grain size also controls the shape of the carbides, rather than that carbide shape is dependent on gamma grain size. When the carbide shape changes from angular to spheroidal form, an increase in fracture grain size is noted. The steels low in chromium and aluminum are more susceptible to the development of round carbide particles.

No relationship was observed in carbide forms obtained below and above the eutectoid inversion temperature.

4. Prolonged annealing in carbon lavite results in surface decarburization at temperatures from 760 to 840 degrees Cent. (1400-1545 degrees Fahr.), producing ferrite. A correlation was found to explain the reason for development of equiaxed or columnar grains in the resulting ferrite. Decarburization of steels having large austenitic grain size generally resulted in columnarization. With small austenitic grains an equiaxed grained ferrite was usually obtained.

It is important to emphasize that the austenitic grain size which controls the nature of the ferrite grains is that of the intermediate partially decarburized austenitic (martensitic) zone, adjacent to the ferrite. As clearly shown in Table IV, this grain size is not always the same as the true grain size of the steel.

5. All steels were fine-grained on annealing at 760 degrees Cent. (1400 degrees Fahr.). At 840 degrees Cent. (1545 degrees Fahr.) steels with low metallic aluminum content coarsened while steels F and D containing 0.025 and 0.011 per cent aluminum remained fine-grained.

DISCUSSION

Written Discussion: By H. A. Schwartz, manager of research, National Malleable and Steel Castings Co., Cleveland.

This commentator's interest in the paper largely centers about the observations with regard to graphitization. The authors have been able to show that the tendency of these steels to graphitize can be related to chemical composition if certain assumptions are made regarding the relative potency of other elements in influencing the rate of the graphitizing reaction.

The authors have gone into no detail as to how they arrived at the numerical value of the several coefficients used in Table VI. This is perhaps wise because these coefficients would admittedly be considered as rounded out approximations. It is quite doubtful whether there would be any general agreement with regard to the approximate accuracy of the numbers chosen by the authors.

The writer's experience would have been that aluminum is relatively much more potent than an equal weight of silicon and that very possibly both aluminum and silicon should be placed at a greater activity with respect to nickel than has been done. The writer might also have been inclined to make a greater difference between chromium and manganese than did the authors. Depending upon the choice of these coefficients the order of graphitizability might have been somewhat altered. The present state of our knowledge as to the joint effect of several elements, all of which individually affect graphitization, probably does not justify too critical a survey of the relative effectiveness of the several elements in combination and the conclusions of the present authors may be filed away among our information on this point.

It is well to mention in the present connection a fact consistent with the authors' observations but not directly referred to in their paper. An effect of a given element certainly varies with the temperature and very probably in some cases varies discontinuously at the critical point, thus it has been known for some years that manganese and chromium even in moderately large amounts retard the graphitizing reaction above the A_1 point much less than below the A_1 point. There is even greater probability that the relative effect of these elements is altered according to the temperature at which the graphitization is to be pursued. Conversely there is some evidence that the element vanadium is more of a retarder at high temperature than at low although this point is not so thoroughly worked out. It is not therefore surprising that a test which explained the authors' observations to their satisfaction above A_1 does not necessarily turn out equally satisfactory below A_1. Whatever else may be said of the coefficients as shown in Table VI it seems quite certain that this coefficient would change in passing through the critical point.

Some years ago Anthony suggested that the graphitization of cementite was always preceded by its spheroidization. The present writer was never convinced that any relation of sequence as to spheroidization and graphitization necessarily existed. It does not appear from Fig. 21 of the present paper that Anthony's contention could be sustained.

It is noted that steels A and B annealed at 840 degrees Cent. for 72 hours contained in the one case graphite and cementite, in the other case graphite alone. We are not given any quantitative information upon which to conclude whether this is due to the relatively high carbon of these two steels, the excess phase representing merely some five or nine hundredths of a per cent of insoluble excess carbon, or whether the authors prefer to ascribe this in some way to a reaction or solution velocity. It would be particularly difficult to ascribe the persistence of graphite in steel B to any such phenomenon since at least in higher carbon alloys it seems rather well established that in order for carbon to get to the place where it is crystallized out it must be

in solution. The graphitization of cementite in situ is certainly a very rare phenomenon and probably does not occur at all. The only means we have for judging the amount of graphite in these samples is micrograph 4, which would seem to represent much more than a few hundredths of a per cent of graphite.

With regard to steel B we have no facts at all. It would furnish an interesting addition to the information imparted to us by the authors if they would supplement their microscopic work with chemical information as to the total and graphitic carbons present.

It may not be amiss to point to the fact that many investigators have had difficulties in rigidly accounting for observed graphitizing rates. The point was alluded to by Dr. Wells a year ago in connection with some of his work on pure iron-carbon alloys and has been frequently encountered by others.

The more work is reported dealing with observed graphitizing rates under controlled conditions the sooner we will be able to formulate a satisfactory hypothesis upon which to base predictions regarding the velocity of this important reaction. The present paper is a contribution toward that end.

Authors' Reply

The authors appreciate the interest Dr. Schwartz has taken in this paper and the discussion he has presented.

The coefficients used for each of the elements as regards their graphitizing potency are the best which we have been able to cull from the literature. These references are given in the bibliography on the bottom of page 15. Such coefficients undoubtedly would change with temperature and be affected by the presence of the other elements; nevertheless, we feel that the substitution of such modified chemical values (Table VI) is preferable to a straight summation of weight per cents (Table V) and this latter is preferable to no summation at all.

The relationship we give on page 16 shows that aluminum was assumed to be two times as strong a graphitizer as silicon. This agrees with Dr. Schwartz's statement that weight for weight aluminum is more potent than silicon. The heading over the fourth column of figures in Table VI was in error in the preprint, reading "Al x ⅔." This is to be corrected to read "Al x 3/2." Undoubtedly this error was the basis of Dr. Schwartz's comment. Because aluminum is present in such small amounts it could have been assumed to be many times more potent, without affecting the order. Likewise it could be assumed that nickel is many times weaker. Any marked changes in the graphitizing effect of manganese, however would upset the order.

Dr. Schwartz points out that the effect of the various elements on graphitization is different above and below the A_1. This is to be expected inasmuch as the solvent above A_1 is austenite and below is ferrite. It will be extremely interesting to know how the chemical analysis affects graphitization below the A_1.

With regard to the necessity of spheroidization preceding graphitization, we must first consider what is meant by spheroidization, and second, we must distinguish between graphitization below and above the A_1. Regarding the

first point, are such structures as those shown in Figs. 15 to 17 "spheroidized" even though angular? If not, what is the name of such a structure? Regarding the second point, Austin and Norris have pointed out that in those steels which graphitize below the A_1 the carbides are round as compared with those steels which do not graphitize. We can see no reason, however, why they should be round.

As shown in Fig. 21 steel A has both cementite and graphite at 840 degrees Cent., steel B has only graphite, and steel F shows neither. Steel A is apparently below the A_{cm} at 840 degrees Cent. with its 1.09 per cent carbon so that both graphite and cementite are present. We have recently completely graphitized a 1 per cent carbon steel below the A_1 and a comparison of the graphite in this steel with that of Fig. 4 indicates that there is less than 0.1 per cent graphite in Fig. 4. Steel B, with 1.05 per cent carbon, was apparently between the A_{cm} and A_{gr} at 840 degrees Cent. and so had graphite but no cementite; the quantity present was the same as shown in Fig. 6. Steel F, which showed neither, was above the A_{gr}, having but 1.00 per cent carbon.

We would like to emphasize one of the points we have been trying to bring out in these recent papers relating to graphitization on prolonged tempering below the critical. Steel B, we think it is, which has the maximum silicon content of the steels treated, 0.44 per cent, has the greatest resistance to graphitization. Silicon is an element we look upon as being most prone to promote graphitization, and steel B, below the critical, is most resistant.

Below the critical range we do not seem to obtain a correlation between the general chemical analysis and the graphitizing tendency of the steel. This morning, however, we have tried to show that the conditions above the critical are quite different, and apparently we do get a correlation between the general chemical analysis and the graphitizing tendency of the steel. Steel B, with a silicon content of 0.44 per cent, is one of the strongly graphitizing steels.

It has been suggested elsewhere by the speaker that aluminum may be the element which tends to promote graphitization at sub-eutectoid temperatures, but further research is necessary before any definite statement can be made. Above the critical point we have shown in the present paper a correlation with the generally accepted ideas on effect of chemical analysis.

SELECTIVE HARDENING WITH THE OXYACETYLENE FLAME

By R. L. Rolf

Abstract

In making possible the surface hardening of parts heretofore considered impractical from a standpoint of size, shape or economy, the oxyacetylene flame has provided the metal working industry with a new tool. This paper discusses this process and data are given on suitable steels and on methods and equipment employed.

WHEN surface hardening is mentioned, one ordinarily thinks of those processes which involve a chemical change in the surface of the material treated. With the oxyacetylene flame a hardened case may be imparted to a steel surface without altering its chemical composition.

For years oxyacetylene flame has been widely employed in the heating of ornamental iron work, pipe bending, blacksmithing, heat treating tools, etc. Recent research has increased our knowledge of its application, developed new controls and has given added impetus to its application to the heat treating industry.

The trend of modern heat treatment has been toward uniformity and neutral gas atmospheres within the furnace; toward accurate temperature control, toward a standardized routing of mass production, insuring that each one of thousands will receive exactly the same treatment. Substituting for these a small oxyacetylene flame without pyrometer control may appear unorthodox and a step backward, however such a supposition does not take into consideration the fact that this flame is the most precisely and completely controlled of all flames. Its temperature, though high, is unvarying and, when correctly adjusted, the gas atmosphere is neutral or reducing and is therefore without chemical effect on the heated metal. In production its action is so rapid, that the operators proceed with a rhythm and smoothness which is the ideal of production engineering.

Many wrong impressions have developed regarding the phrase "hardening with the oxyacetylene flame" and it may be well to

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examine and study certain aspects of this method of heat treating. This phrase does not mean the firing of heat treating furnaces with acetylene gas, and while this has been proposed many times where high temperatures have been desired, it has always been discarded in favor of cheaper gas or oil in a properly designed furnace; then too, the intense oxyacetylene flame would quickly soften and erode the refractory lining.

Heat treating with the oxyacetylene flame does not mean case hardening with acetylene gas, as this gas is not a desirable carburizing material, furthermore, it tends to change its chemical nature spontaneously with liberation of large quantities of heat when exposed to high temperatures and pressures.

This method of hardening imparts a hardened layer to the surface of the material without altering its chemical composition. Since no chemical change is effected in the surface of the material, this process must be differentiated from those which require the absorption or addition of other elements, such as carburizing, nitriding, cyaniding, etc.

These latter processes require prolonged heating at high temperatures in special furnaces, thus making many jobs prohibitive, from a standpoint of size and shape. The long time cycle at elevated temperature often results in excessive distortion involving expensive straightening operations or costly machine work, with the necessity for allowing ample stock to take care of this anticipated distortion.

In many instances only portions of an object require hardening, and in such cases it appears wasteful; for example, to heat a 7000-pound body to a temperature of 1700 degrees Fahr. for a period of 90 hours when only about 10 per cent of it requires hardening. For mass production of small parts which are to be uniformly hardened, the furnace method is probably the most economical, but there are instances where parts are of such proportion that they become too bulky to handle by the furnace method. Some designs are such that there is danger of distortion or cracking when using the furnace method. In such instances the acetylene flame may well be used to advantage, since that process permits the hardening of any accessible portion of an article with no measurable distortion.

This oxyacetylene process employs the use of a standard welding blow pipe, the standard welding tip being replaced with a specially designed multi-tip or multi-flame head which locally heats the surface of the object being treated. A cooling arrangement either

incorporated in the head or designed to closely follow the torch, cools the heated part of the object as fast as it is brought to the desired temperature.

This method produces no scaling or pitting and the hardened surfaces are left clean and smooth, but precaution has to be taken, because a temperature of 6300 degrees Fahr. is applied at a distance of only ¼ inch from the surface we desire to heat to a temperature range of only 1450 to 1550 degrees Fahr. Positioning the flame too close to the work, or applying it for too long a time, may result in searing or burning the surface material and producing a brittle and coarse underlying grain, or it may result in overhardening and surface checking.

Unless the section being treated is exceptionally small this treatment will not affect the entire area but will be confined to a depth ranging from a mere skin to a maximum of ¼ inch.

The rate of heat induction is an important factor. The torches must not move too slowly to cause burning of the surface, nor must they be moved too rapidly as the proper depth of penetration could not be obtained. An efficient and satisfactory rate has been found to be between 4 and 6 inches per minute.

Heat conduction is as important as heat induction. Quenching solutions are employed to dissipate heat from the surface of the object being hardened so as to develop certain desired properties in the metal, these properties generally being crystalline refinement, increased strength and increased hardness.

Heretofore when reference was made to quenching, one pictured a heated mass being plunged into a liquid bath. Flame hardening alters this picture, for the part is quenched as rapidly as it is heated and only a small area, shallow in depth, is heated at one time.

As we review the mechanism of quenching employed in this process, we find several varied forms of application starting with the earliest form arrangement whereby the object, such as a gear, is suspended directly over the quenching tank, and as each tooth is heated the object is rotated so as to bring the next tooth in line with the torch and at the same time immerse the heated tooth in the liquid quenching bath.

It is only a short step from this procedure, to the rotary method of heating small objects, where the components are rotated in front of one or more torches and when they have reached the desired temperature they are rapidly ejected into a cooling bath.

In rotary hardening of large circular sections or on straight line progressive hardening, some arrangements use a small water jet directly behind the torch (Fig. 1). While this set-up will produce satisfactory results, the ideal method is where the torch head is designed for both heating and cooling as illustrated in Fig. 2. With this arrangement, the head is divided into two compartments, the forward portion acting as a heating element while the rear orifices are designed to handle the prescribed quenching medium.

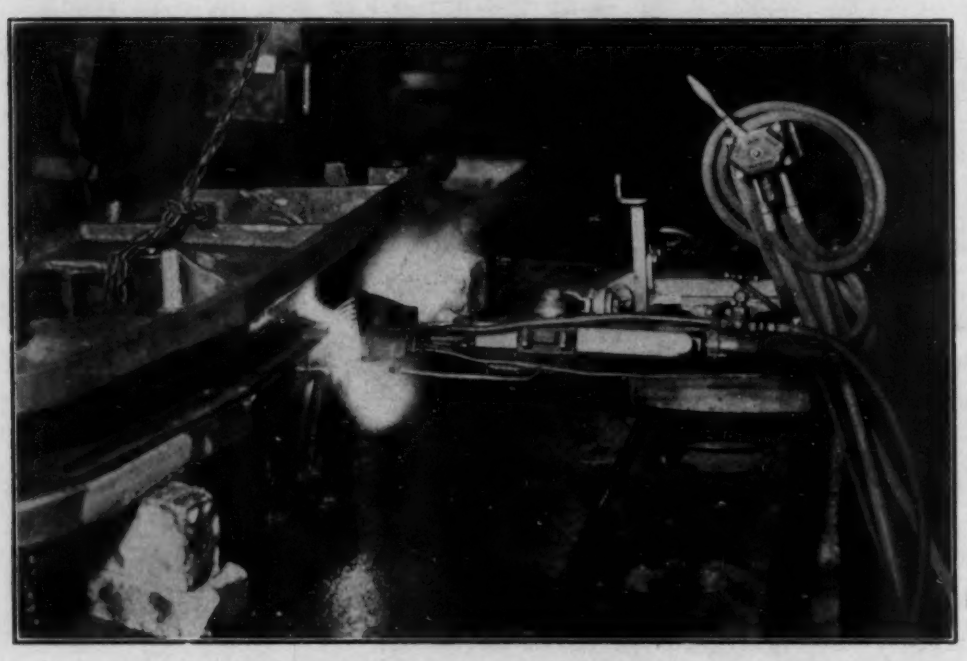


Fig. 1—Photograph of Quenching Nozzle Directly Behind Heating Torch.

The most common types of quenching media include (1) water and aqueous solutions of salts, acids and alkalies, and (2) mineral, vegetable and animal oils. Using still water at 68 degrees Fahr. as a base unit for comparing quenching rates, the A.S.M. quotes as follows:

Quenching Media at 68 Degrees Fahr.	Quenching Rate
Still water	1.00
Still 5 per cent sodium chloride	1.12
Still 5 per cent sodium hydroxide	1.17
Still 5 per cent calcium chloride	1.06
Still mineral oils (Vis. 75-250)	0.17 to 0.36
Still vegetable oils (Vis. 200-1500)	0.15 to 0.37
Still animal oils (Vis. 130-270)	0.19 to 0.35

Of all the quenching media, water is the most convenient, but as the temperature is increased the rate drops, and at the boiling point

the quenching power falls to about 10 per cent as compared to water at 68 degrees Fahr.

A more efficient quench is found in sodium chloride solutions. Five and ten per cent solutions are the concentrations more commonly used. Stronger concentrations are often recommended but are to be avoided. These solutions have the disadvantage of causing rapid corrosion and it is essential that all parts be completely rinsed after quenching. Sodium hydroxide solutions are about on par with the

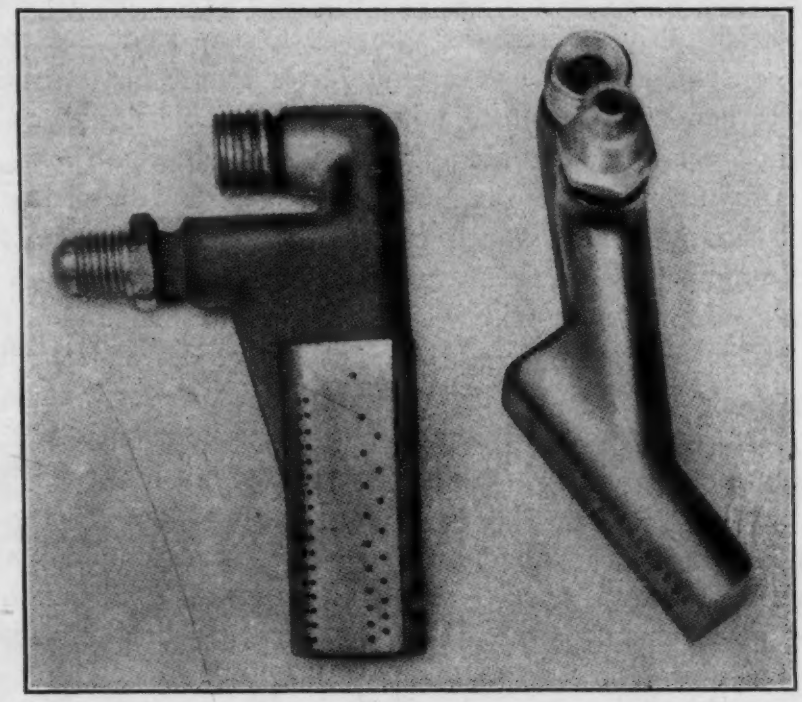


Fig. 2—Flame and Water Orifices Incorporated as a Unit in the Straddle-Type Heads.

chloride solutions, but instead of corroding, they give a bright finish to the material. In using this medium, only solutions of low concentration are to be recommended as these solutions cause skin irritation and require special handling.

The aqueous solutions all have a fast cooling rate and on account of this, they are strictly confined to the carbon steels of low or medium carbon, or the alloy steels possessing a low or medium carbon content.

The oils have about one-fifth to one-third the cooling rate of water and will produce less distortion and less residual stress and make an ideal quenching medium for complicated shapes and steels of high alloy content.

Except for rotary quenching of small objects, where the parts may be ejected into the bath, the quenching media used in torch hardening are confined to the aqueous type, thus, for the present, we are more or less confined to the more rugged analysis in the water quenching category.

It should not be misconstrued from the preceding paragraph, that the process is entirely limited to water and solution quenching steels, as other analyses have been successfully treated, but this is usually accomplished by the use of extreme care, or by the employment of trick quenches, such as sprays, air, soap solutions, etc.

Carbon content is the governing factor in the heat treating of straight carbon steels and to obtain any appreciable degree of hardness, the material should contain at least 0.35 per cent carbon. Raising the carbon content increases the resultant hardness, but there is a limit of carbon content which can readily be solution quenched. Steels containing 0.60 per cent carbon or greater may be torch hardened but care must be exercised to prevent surface cracking or checking. The low carbon alloy steels are the most desirable to harden by this method whereas the higher alloy steels present a more complex problem and many in this category are to be avoided. Table I lists many of the steels which may be successfully hardened by this procedure.

Fine grain steels with only a slight abnormality and having a McQuaid-Ehn rating of 6-8 are preferable, as this combination develops a martensitic structure in the hardened zone without the usual martensitic cracks.

Since flame hardening is only surface hardening and only a comparatively thin layer is treated, it is of the utmost importance that this surface be in the proper condition to successfully respond to this operation. Decarburized zones are to be avoided. The components must have the requisite carbon content at the surface as well as underneath.

The surfaces to be hardened must be scale-free as scale retards the quench and maximum hardness will not be attained. Pits, blow holes, seams and laps, are material objects which are to be avoided as these most generally result in the formation of large surface holes, or develop into cracks during the quenching operation.

When selecting steels to be hardened by the oxyacetylene flame method it should not be overlooked that this process changes the structure of the outer fibers only. As there is no hardening from $\frac{1}{16}$

to 3/8 inch below the surface, expensive alloy steels should not be used unless they are to be quenched and tempered prior to the torch hardening operation. This operation imparts a wearing case only, and in no way does it alter core strength. Many instances may be cited, where manufacturers have replaced highly stressed parts fabricated from quenched and tempered alloy steels possessing high physi-

Table I
Steels That May Be Successfully Hardened by the Oxyacetylene Flame Method

S.A.E. No.	C	Mn	Cr	Ni	Mo	Va	Si
1000 Series	0.35–0.60	0.60–0.90	.....	.....	.....	.....	.....
1300 Series	0.25–0.40	1.25–1.90	.....	.....	.....	.....	.....
3100 Series	0.25–0.45	0.50–0.90	0.45–0.75	1.00–1.50	.....	.....	.....
3200 Series	0.25–0.45	0.30–0.60	0.90–1.25	1.50–2.00	.....	.....	.....
3300 Series	0.25–0.45	0.30–0.60	1.25–1.75	3.25–3.75	.....	.....	.....
4100 Series	0.25–0.45	0.50–0.90	0.50–1.10	.....	0.15–0.25	.....	.....
5100 Series	0.25–0.35	0.30–0.60	0.60–1.10	.....	.....	.....	.....
6100 Series	0.25–0.45	0.30–0.90	0.80–1.10	.....	.....	0.15–0.25	.....
Cromansil	0.25–0.45	1.00–1.20	0.40–0.60	.....	.....	.....	0.80–1.00

cal properties but with rather low surface hardness, with a carbon steel as-forged or as-cast flame hardened unit having a high surface hardness but low physical characteristics of the core. Substitutions of this type usually result in premature failure and the condemning of the flame hardening process.

Wherever possible, flame hardening of steels in the as-cast or as-forged condition should be avoided. For best results the parts should be heat treated by either quenching or tempering to a sorbitic structure, or by normalizing to produce a grain size which closely approaches the heat treated structure.

Flame hardening a part that had been in service should never be done unless the part had been annealed to relieve all working stresses prior to the hardening operation. Flame hardening sections which have been already torch hardened, in an attempt to improve on the first operation, may often lead to disastrous results, unless the section is annealed prior to the second treatment.

The degree of hardness obtained is between 400 to 700 Brinell or 56 to 90 Shore, depending upon the analysis of the material, size of section and speed of operation. This hardness is maintained through about 80 per cent of the depth of the hardened area. The core is not affected and there is no rapid falling off of the hardness, the transition from case to core being gradual (Fig. 3). Instantaneous pressure quenching following the flame produces a bond between the hardened area and the core.

A sharp line of demarcation between these two zones is not observed as the hardened zone and the core gradually blend without any marked precipitation of free ferrite either in or below the gradation zone, thus flaking and spalling under service stresses are avoided.

This process may be adopted to both castings and forgings. The size of either is not a limiting factor and if the part is fabricated from material of the proper analysis, and the sections which require hardening are readily accessible, then the part may be flame hardened.

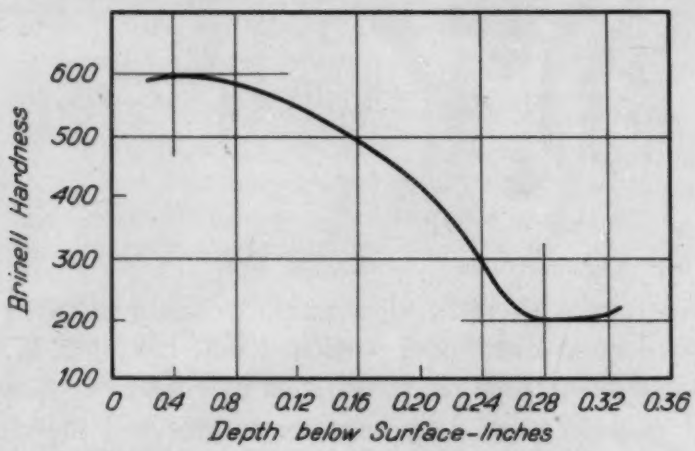


Fig. 3—Curve Showing that the Hardness Transition from Case to Core is Gradual.

Flat sections, circular paths, irregular shapes and varied combinations may be successfully hardened by this method. These varied shapes place the hardening procedures into several classifications according to the direction of movement of either the part being treated or the movement of the torches along the work.

This classification may be generally divided into the four following groups:

1. *The stationary or spot hardening method.* During this process the torch and work are stationary during the treatment.

2. *The progressive method,* where the torches travel along the face of the object, such as gear teeth, track rails, etc. (Figs. 4 and 5).

3. *The spinning method.* On circular hardening the specimen is spun or rotated in front of a stationary flame. This method may be subdivided into two parts according to the speed of rotation:

(a) Where the part is rotated very slowly in front of a stationary flame. This method usually leaves at the starting and stopping points a narrow oblique path which is generally two or three points softer on the Rockwell than the adjacent hardened areas. This

method is used on large circular sections such as track wheels, sheaves, bearing surfaces, etc.

(b) This subdivision covers the spinning of the work at a fair rate of speed (between 70 to 150 revolutions per minute) in front of one or more torches. When the entire area has reached the proper quenching temperature, the rapidly rotating specimen is quenched by permitting it to spin under a cooling spray or by ejecting the part from the machine into a prescribed coolant. This method is employed in the hardening of small parts, such as small rollers, pinions with small teeth, etc.

4. *The combination method,* which combines both the progressive and spinning methods and is applied to rounds where a considerable area is to be heated. In this method the work is rotated before a blow pipe which gradually traverses the specimen longitudinally.

Equipment

There are several types of flame hardening machines used in the United States, the Monitor construction, Sykes machine, the Gleason design and the Universal type.

The Monitor type, probably the most widely used for progressive hardening, consists of mounting the torches on one of the standard oxyacetylene cutting machines. The speeds used in torch hardening coincide with those obtained on the cutting machines, thus making this an ideal traversing device.

Variable speeds of travel on all types of machines permit uniform treating of sections of different sizes and tapering cross sections.

For general application the equipment consists of a large capacity water cooled oxyacetylene blow pipe and various types of water cooled multi-flame heads which pass about 300 cubic feet of each gas per hour. There are many applications where this large capacity head is not applicable, as on small work. In such cases a smaller mixer is all that is required.

In gear hardening the head is designed to allow operation in the restricted area between the teeth.

Although it has been the practice until quite recently to flame-harden the opposite sides of each tooth separately, the desirability of perfecting a method whereby both sides of the tooth could be hardened simultaneously has long been apparent. This has led to the development of "straddle type" heads that make simultaneous treatment possible.

Foremost among the advantages of the new method is that the gear may be hardened in one-half the time formerly required. In addition to time saving there are two additional advantages of the method over that of hardening each side separately.

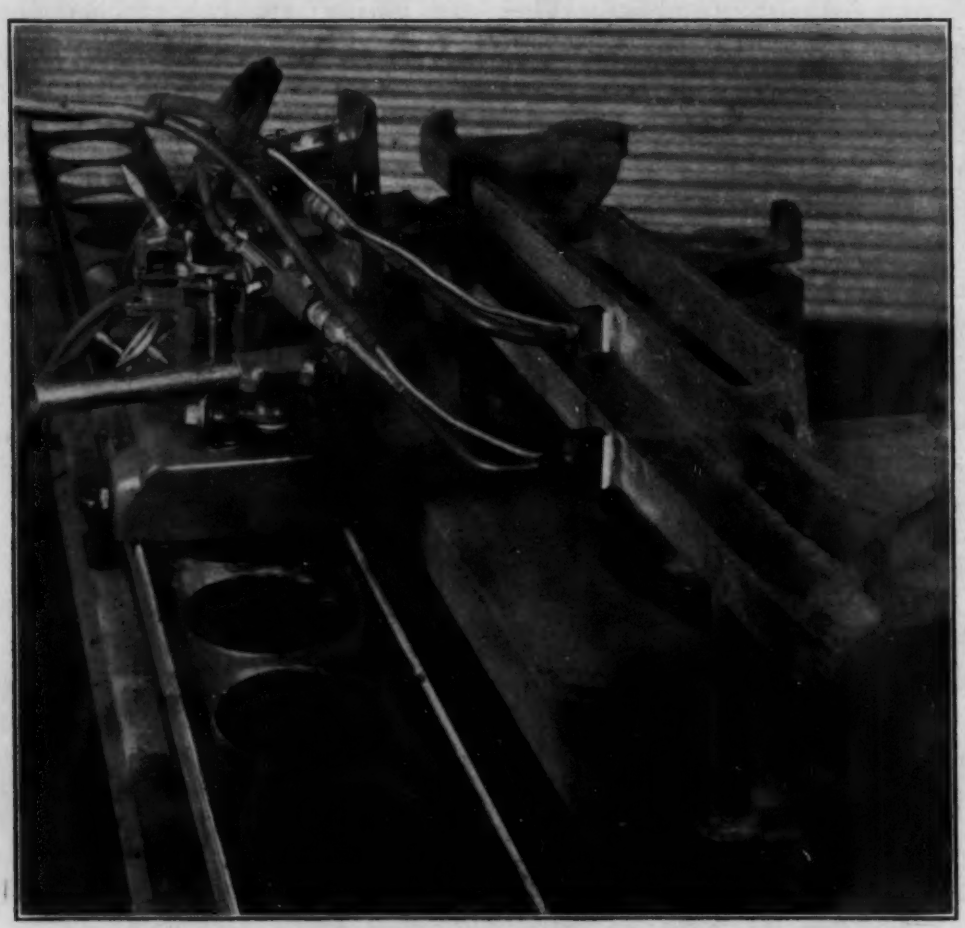


Fig. 4—Photograph Showing the Progressive Method of Torch Hardening Where the Torches Travel Along the Face of the Object.

1. The elimination of the softening of the first side of the tooth treated. With the old method, heat applied to the second side of the tooth had a tendency to soften the side already treated. In contrast, the simultaneous application by the straddle method leaves both sides of the tooth hardened uniformly.

2. Distortion as the result of single sided treatment is eliminated. Because the straddle method provides for heat and quench striking both sides of the tooth simultaneously, the tendency for small teeth to distort is overcome.

These heads are used in pairs, a right-hand and a left-hand head

making up a set. This combination is not strictly confined to gear teeth but the heads can be used for the hardening applications such as splines, keyways, wobbler ends, grooves, etc.

Their small size allows exact portioning in limited spaces thus permitting more accurate control in directing the flame towards the portions of the tooth surface desired to be treated.

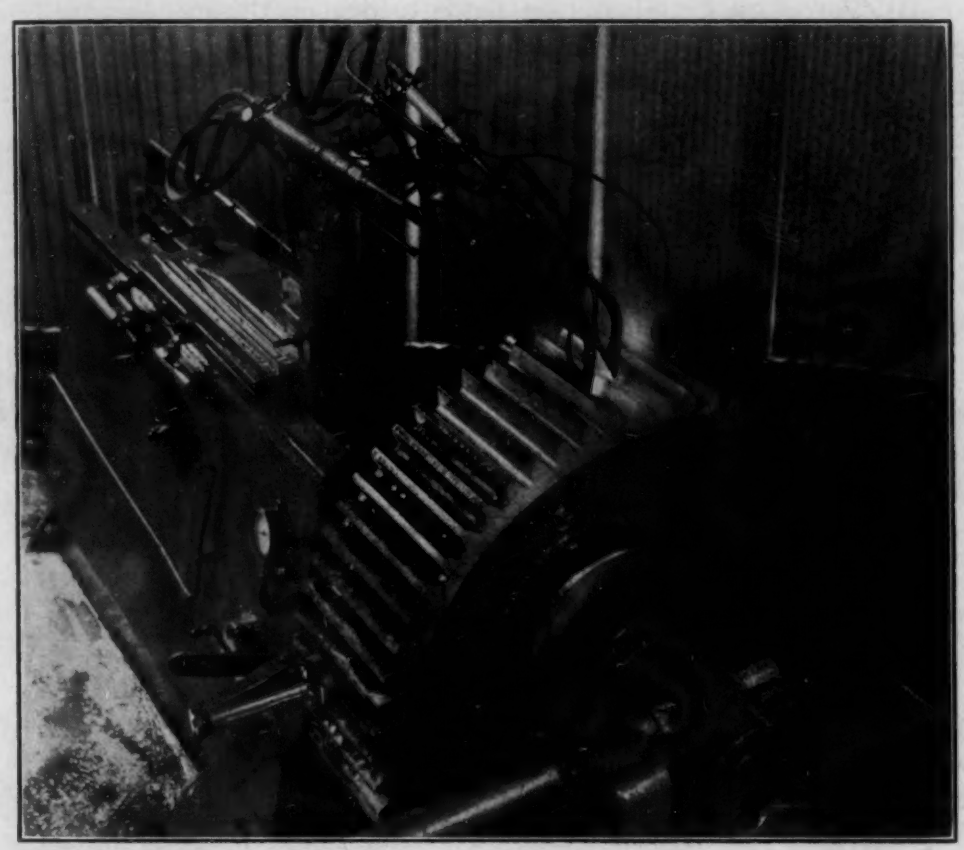


Fig. 5—Photograph Showing Torch Hardening of Both Sides of a Gear Tooth Simultaneously.

Good workmanship is easily attainable, as an exact relationship between the heating and quenching is constantly maintained by the flame and water orifices incorporated as a unit in each head. In addition, the arrangement of the heating orifices compensate for varying thicknesses of the tooth and assures a symmetrical case. The closer spacing of the orifices at the bottom of the head gives the greater concentration of heat where the surface is backed by the greatest mass of metal.

To insure equal hardness and contour on each side of the tooth, the distance from tooth faces to head faces must be equal, and the

flame intensities and gas ratios the same. The leading flames of the heads must arrive at the entering end of the tooth at the same time.

Care should be taken to avoid overheating the tooth at the start of the operation. The time required for the quench to strike the edge of the tooth after the machine has been put into motion may be sufficient to overheat the tooth if the starting point is too long.

Too great an initial preheat tends to deepen the case across the entire tooth.

Quenching pressures are important, especially on the small tooth sizes. Too much pressure will interfere with the flames, and too little pressure may not produce sufficient hardness.

Size Head	Oxygen Pressure Lb. Per Sq. In.	Acetylene Pressure Lb. Per Sq. In.	Quench Pressure Lb. Per Sq. In.	Operating Speed in. Per Min.
1 D.P.	28	5	8	4½
2 D.P.	40	5	3	4½
3 D.P.	17	5	1.5	5

When treating gear teeth of sizes other than those indicated in the table, select the head which gives the best coverage to the tooth face. The head size number will usually be larger than the gear tooth D.P. For example, 2½ D.P. gear teeth may be hardened with 3 D.P. heads using a lower operating speed than the speeds indicated in the table.

Stress Relieving

Tempering or stress relieving is absolutely essential and should follow closely after quenching. This operation is performed in a standard type heat treating furnace or air or oil bath at temperatures not to exceed 400 degrees Fahr. This low temperature is sufficient to relieve the stresses set up by quenching but has very little if any effect on the hardness. After this tempering operation the work may be removed from the furnace and cooled in still air or may be furnace cooled if desired.

DISCUSSION

Written Discussion: By J. T. Howat, metallurgist, American Spiral Spring and Manufacturing Co., Pittsburgh.

In covering this process of heat treating Mr. Rolf has prepared an excellent paper in a thorough and practical manner. After reading the paper over and being requested to make some comments on same one finds that there appears to be very little left to say except to offer congratulations to the author.

The careful application of the process cannot be too fully stressed as the improper use of the oxyacetylene flame (when the process is first attempted) has resulted in some very unsatisfactory results being obtained.

It is gratifying to note the importance placed on the need for careful setting up of the torch tip to the surface to be hardened and the time factor required to obtain the correct amount of heat in the surface metal and the proper degree of quenching.

When it is desired to obtain a greater depth of hardness, than say $\frac{3}{16}$ inch, it is necessary to apply more heat to the surface either by increasing the size or number of holes in the tips. This will naturally impact more heat into the body of the steel and there will be more distortion after heat treating than is usually experienced. To keep this distortion to a minimum, full strain relieving heat treatments should be given to the part before flame hardening and while hardening it should be immersed in water as much as possible. The main idea being to reduce the amount of this body heat to the minimum.

As the process calls for balanced and standardized operating conditions for each respective part to be heat treated, we should not lose the fact that our source of fuel must be such as to give a constant supply of gases at uniform pressure. To do this a 3 or 5 cylinder manifold system for the gases is required, and a constant water supply, unaffected by the other demands of the plant for water.

The list of steels shown in Table I covers the range of steels that can be successfully flame hardened, and as stated by Mr. Rolf increasing care must be taken in the process of hardening as we change from the medium carbon steels to the higher alloy steels.

With the alloy steels a quick preliminary preheating of the surface and a gradual tapering of the heat and quenching action towards all corners will help to eliminate surface cracking.

Where the slower quenching mediums are used one must apply a general quenching effect on the rest of the part to keep down the steady building up of residual heat in the part being treated. The type of equipment, and method of applying the heat and quench is always governed by the piece being treated and results desired. It should be noted that if the size or number of holes in the torch tip is too small for the surface being treated we will develop excessive body heat before obtaining the correct surface heat, which condition is unsatisfactory and uneconomical.

With the conditions reversed, i.e., too much heat being applied to the surface we obtain a coarse grain, surface cracks and possible burning of the surface metal.

When the surface is heat treated in the progressive method, care must be taken that the merging of the treated areas does not overlap too much or there will be double quenching which will result in surface cracks.

It is suggested that, where possible, a tempering treatment of 400 degrees Fahr. be given the parts after surface hardening.

It has been a pleasure to read this paper and offer a few comments, and I believe that Mr. Rolf should be highly complimented for this fine piece of work.

Written Discussion: By R. P. Donnell, metallurgical engineer, The White Motor Co., Cleveland.

The subject of this discussion is not particularly new, rather it is due to increased application resulting from more recent research that makes the subject of flame hardening extremely interesting not only from an academic standpoint but from the practical industrial standpoint as well.

We have for some years been familiar with the advantages of speed, economy, freedom from distortion, etc., on many small jobs found in either the heat treat or blacksmith shop. At the White Motor Co. factory we have used this method to advantage on such parts as valve tappet adjusting screws, camshaft thrust screws, valve stem thrust caps, and transmission side plates. But when we review the possibilities that are opened by recent development, we look upon the process with renewed interest.

Mr. Rolf, in his paper, has not definitely indicated it as such but I think that one of the most important features of the process is that it reduces distortion to a negligible degree on many jobs which would be prohibitive from this point alone. At the same time, neither should we minimize the importance of ultimate cost savings which result from speeding up work in the factory, more economical use of materials, and all the contingencies which these include. Other advantages to be noted are—

1. Reduced scrap losses, as the quality of work from the process is uniform and accurately controlled.
2. Reduced cleaning costs.
3. Less expensive steels may invariably be used.
4. The equipment can be moved to work that ordinarily cannot be accommodated by the usual hardening methods.

Another major advantage, which I believe will result in wider acceptance of the process, lies in the fact that core properties may be developed by usual hardening methods that are fully retained after selective flame hardening. In the case of gear steels, whereas we are now using, and limited to, a high alloy carburizing type, carburized and heat treated to an elastic limit of 105,000 to 135,000 pounds per square inch, and all design combinations are limited to this figure, we may, with this new process, substitute a much less expensive type of steel and develop an elastic limit of 150,000 to 175,000 pounds per square inch with all other advantages included.

As regards the selection of steels for flame hardening, Mr. Rolf has given us a table of those which may be successfully hardened by this method. We are all familiar with the fact that certain types of steel, even though others may be substituted, are best suited to a given purpose. I would like to raise a point for further discussion by asking if it is known what steels are best suited to a particular method of the flame hardening process. For example, if an S.A.E. 6140 steel can be hardened by any of the classified methods, such as spinning, etc., will another type, such as S.A.E. 3140 or 6195, be limited to one of the methods?

Written Discussion: By Roger O. Day, metallurgist, Process Development Laboratory, Linde Air Products Co., Newark, N. J.

In his discussion of the flame hardening process, Mr. Rolf has presented

much information of importance and interest. It is felt, however, that certain of the points presented might well be emphasized and enlarged upon to a degree not possible in the space allotted to the paper. This discussion is, therefore, submitted not in a spirit of criticism, but rather as a supplement to that already presented by Mr. Rolf.

The first point to be emphasized is that the flame hardening process is definitely not one for haphazard, hit-or-miss operation, but is conducted under controlled conditions that permit a high degree of consistency in results from piece to piece. It is not to be denied that the human element plays a part, but any operator of average intelligence who exercises a reasonable amount of conscientious care in his work can be expected to produce satisfactory and consistent results in flame hardening. The most important factor in obtaining the best results is mechanization of the process to the greatest possible degree. Further than that, many applications are adaptable to automatic control to such an extent that the operator's only duties are to position the heating heads and then press a starting button to start the operation. Users of the process are strongly urged to install automatic control where possible, particularly where there is a high degree of repetition in the type of part treated, and certainly all users of the process should make flame hardening operations as mechanical as possible, even though manually operated.

In his discussion of quenching media, Mr. Rolf points out the comparative efficiencies of various liquids. The data presented, however, deal with still baths whereas the vast majority of flame hardening applications involve the use of a spray type of quench. It has been the experience of this discusser that the efficiency of a more or less finely divided spray quench operating under normal water line pressure is at least as high as a bath of brine or caustic solution. It thus appears that there is a questionable need for brine or other salt solutions, where quenching efficiency only is desired, if a properly designed and operated spray quench is used.

The use of oil as a flame hardening quenching medium in operations other than those in which small parts can be quickly ejected from a machine into a bath of oil, creates a fire hazard not to be tolerated. However, the need for a liquid quenching medium safe to use in the vicinity of the flames, and one that will give a quench approximating that of oil, is frequently encountered. Good results have been obtained by the use of soluble oils in water or a solution of soap in water. Then, too, in the treatment of some alloy steels the efficiency of a properly used air spray is surprisingly high.

This writer wishes to further stress the point brought out by Mr. Rolf in the last paragraph of page 48 of his paper, which refers to the failure of under-designed flame hardened parts. Too frequently does the design take into consideration only the increased properties of the flame hardened case to the neglect of the core properties. If the operation of the part in question is such as to require an alloy steel of certain high physical properties before flame hardening, certainly the same core properties are necessary in the flame hardened part. It must be borne in mind that the increased life of a flame hardened part is due to its greater resistance to wear and not to its increased core strength.

Written Discussion: By A. K. Seemann, engineer, Linde Air Products Co., 30 E. 42nd St., New York City.

Mr. Rolf's paper has been read with considerable interest and in offering the following comments it will be noted that the discussion is quite in agreement with Mr. Rolf's presentation but differs in the degree of emphasis placed on certain topics.

Most flame hardened articles are quenched with cold water. Sensitive steels are sometimes air quenched and in some cases quenched with soluble cutting oil and water or soap solutions. So far, it has not been necessary to consider salt or caustic solutions because a water spray under ordinary city pressure is sufficiently drastic. Oil is inadvisable because of the fire hazard.

It is felt that further emphasis should be placed on the importance of steel selection for flame hardening applications and that quite as much care be used in selecting pre-treatment for core properties as is exercised in the flame hardening operation. Flame hardening does not offer the opportunity to substitute straight carbon for alloy steels but rather enables the engineer or designer to furnace heat treat for maximum core properties and flame harden for surface properties. Too often attention is riveted on surface hardness alone and little or no attention is given to the physical properties of the core. Straight carbon steels will develop the desired surface hardness but obviously this is but one factor in the selection of a steel for a particular service.

Oral Discussion

C. F. MERRILL:[1] I would like to ask the speaker if he can tell us something about this method of heat treatment on iron castings of any of the well-known types.

R. L. ROLF: Our cast iron has been heat treated with great success in many instances. If the iron is of such a nature that it will not take a quench, then it is useless to try to harden by the flame hardening or any other means of hardening. With the high strength cast irons—such as chromium-nickel or chromium-molybdenum, or even malleable iron—if they have been properly cast they can be successfully heat treated, as we have done in many instances.

Is there any specific type?

C. F. MERRILL: Not particularly, except the gray irons of relatively low silicon.

R. L. ROLF: Irons in the furnace casting class, grate bar castings, etc., have not been hardened very successfully. Some will respond and some will not, but the high strength alloys can usually be hardened successfully.

HOWARD SCOTT:[2] There are a few questions I would like to ask Mr. Rolf about flame hardening processes. We have been involved at a little different angle on very large work.

What do you do to control grain coarsening? How do you know, once you start the flame progressing over the work, that it is set to give you the right depth of hardening, and whether you are hardening at all?

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[1]Engineer, Draper Corp., Hopedale, Mass.

[2]Research Department, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

Do you know anything about the actual surface temperature? How hot does the surface get? What is the nature of the distortion? In what direction do you get distortion? Normally, you would expect surface hardening to put the surface in compression because it is then of less density, but we have evidence in the opposite direction. Can you confirm that observation?

R. L. ROLF: Mr. Scott's problem, is different than anything in my experience due to the fact that he is handling extremely large sections as compared to ours of more practical size.

As far as grain size is concerned, we try to regulate our flame so the hardening temperature does not exceed that specified for the material which is being treated. He states, "How do we know when the temperature is reached?" We have no pyrometer control—that is true. After a man has been in the practice for a while he can gage his temperatures fairly accurately. If the part is started out at the proper temperature and the speed of the torches is increased to compensate for the induced heat as it moves along the surface, we will find that at the finish of the work there will be approximately the temperature as we had at the start.

However, if we intend to pour the heat in very rapidly, say 1700 degrees Fahr., when it should only be heated to 1475 or 1500 degrees Fahr., we are going to coarsen the grain, and as we proceed along we are going to build up our heat to a point where the finishing temperatures will be in excess of what it should be and the grain size is going to be abnormal.

Distortion is hard to govern. I doubt whether any man without having any previous experience on a job can predict the nature or direction of distortion. On heavier size sections where the bulk is such, that heat is not of vital importance to warp the specimen, we are safe, but on thin sections of variable cross sections we cannot determine the degree of warping that the piece will undergo.

HOWARD SCOTT: How deep do the grains coarsen?

R. L. ROLF: We coarsen to a depth of about a quarter of an inch, with an extremely coarse brittle condition on the surface. If the speed is regulated and the flames reduced and the gas mixture is properly regulated then the coarsening does not penetrate that deep and we have a regular heat treated structure.

HOWARD SCOTT: How far away from the work have you set your flame?

R. L. ROLF: About ⅛ to ¼ inch, depending on the work.

HAROLD J. STEIN:[3] In answer to Mr. Scott's question relative to the knowledge of the hardness obtained in flame hardening during operation and also the microstructural characteristics, I would like to mention a procedure followed at Allis-Chalmers Company where the part being hardened is a costly part such as a large forging.

We forge a prolongation on the forging approximately the same diameter as the part to be hardened and then after machining we proceed to harden the prolongation by making hardness test and structure surveys over a short length, say 1 inch, of the surface on the prolongation. In this manner it is possible to make adjustments relative to temperature of flame and speed of

[3]Research engineer, Allis-Chalmers Manufacturing Co., Milwaukee.

travel of the torch so that eventually you obtain the metallurgical characteristics desired. With this data, you can then proceed to harden the forging with controlled flame and speed as indicated in the hardening of the prolongation. I am discussing the procedure on forgings of about 40 inches in diameter.

Author's Reply

Referring to Mr. Donnell's question regarding reduced scrap losses—this is probably one of the mainstays of this process. We do not receive the distortion, thus we do not get the scrap loss that is associated with the batch type furnace. Parts which were too thin in one section and too bulky in another, warped excessively in the batch-type method of quenching. In flame hardening we can select the point we wish to harden and heat and quench that point only and produce a very satisfactory job.

Reduction in cleaning cost is another important factor because we do not have the scale to contend with, and pickling or sand blasting operations are eliminated as the work comes out very clean.

Less expensive steels may be used, and that is another point in favor of the flame hardening process. We can produce a surface hardness without going to the expensive alloy steels; and you substitute in many of these cases S.A.E. 1040 and 1045 in place of S.A.E. 4615, 3115, etc., provided of course we do not have to maintain their respective core strength.

There are cases where the engineer forgets about the core properties, and he will use an S.A.E. 6145 analysis and heat treat the piece and put it into service around 400 Brinell. When he changes to flame hardening he forgets about the physical properties of the core and he substitutes an S.A.E. 1045 steel unheat treated, because the surface hardening will give him the hardness he is after. He does not have his physical properties and the part fails in service. In another case, the man uses an expensive alloy steel to produce surface hardening when he does not need the core properties of an alloy steel.

With regard to the selection of the steels for flame hardening, at the present time I would like to see it confined to the more rugged type or the water quenching steels.

With reference to the S.A.E. 6140 steel—we have hardened gear teeth, cams, and other sections fabricated from this analysis with very satisfactory results, but you cannot do it very successfully with a water quench, but you can do it with a soluble oil quench.

The S.A.E. 3140 analysis is practically the same thing. If the carbon is on the low side of the range you can get by with a water spray quench. If it is on the high side of the range, we would prefer the soluble oil quench.

THE EFFECTS OF FIBER ON THE NOTCH TOUGHNESS OF MILD STEEL AS INFLUENCED BY COOLING RATE

By O. W. Ellis and J. E. McDonell

Abstract

Howe's definition of fiber is quoted and reference is made to the work of Kirkaldy, Charpy, Brearley and others on the effects of fiber on the mechanical properties of steel. Experiments are described having for their object the determination of the effect of cooling rate and actual grain size on the notch toughness of a steel in directions transverse and parallel to the direction of its rolling. An attempt is made to explain the results of these experiments, the suggestions being made that the reduction in the notch-sensitivity of this steel brought about by quenching is due largely, if not entirely, to an increase in its cleavage strength and that the effects of fiber in this steel must be to reduce its resistance to plastic flow rather than to alter its cleavage strength.

THE influence of the direction of working on the mechanical properties of iron and steel has been the subject of considerable investigation, and the importance of fiber has been recognized for many years. Howe, in his work[1] devoted two out of thirty-two chapters to a consideration of the origin and effects of fiber. He defined fiber in the following terms:

> "Fiber implies some longitudinal heterogeneousness. Wood is fibrous because it is stronger lengthwise than crosswise, and this in turn because it has certain internal longitudinal surfaces of weakness. When bent greatly it tends to yield by longitudinal shear, that is by the shearing or sliding of one fiber over another. This excess of longitudinal over transverse strength

[1] "The Metallography of Steel and Iron," (McGraw-Hill Co., Inc., New York City, 1916).

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, O. W. Ellis is director, department of engineering and metallurgy, Ontario Research Foundation, Toronto, Canada, and J. E. McDonell is undergraduate student, Queen's University, Kingston, Ont.; research assistant, summers of 1936 and 1937, Ontario Research Foundation, Toronto, Canada. Manuscript received June 24, 1938.

of the mass as a whole I take to be the essence of fiber. It has two aspects, the excess of longitudinal strength and the deficit of transverse strength.[2] Of these the former is usually the cause of the merit of fiber. We value a fibrous wood not because of its relatively small transverse strength but because of its absolutely great longitudinal strength.

"There are indeed certain cases for which the deficit of transverse strength is in itself a merit. Were a rope as strong crosswise as lengthwise it would lose that flexibility which makes it useful for purposes for which an equally strong wooden or metal rod would be uselessly stiff.

"In the absence of any agreement on the subject I propose to call all systematic differences between the longitudinal and the transverse structure and properties 'fiber,' whether these differences are properly regarded as giving longitudinal strength or transverse weakness or brittleness. All excess of longitudinal over transverse strength, and all tendency, whether developed or dormant, to break with a longitudinal or fibrous fracture, may be referred to fiber in this sense of the word."

Kirkaldy[3] was one of the first, if not the first, to make quantitative determinations of the effects of fiber upon the mechanical properties of various materials. The numerous conclusions, 66 in all, at which he arrived in the course of his classic enquiry, were presented collectively in the last section of his book, and from them are quoted here those pertinent to our subject.

"10th. The breaking strain and contraction of area of iron plates are greater in the direction in which they are rolled than in a transverse direction, ...

"12th. The breaking strain and contraction of area are greater in those specimens cut lengthways out of crank-shafts than in those cut cross-ways, ...

"17th. The breaking strain and contraction of area of *puddled*-steel plates, as in iron plates, are greater in the direction in which they are rolled; whereas in *cast*-steel they are less,[4] ....."

Nick-bend tests were in common use in Kirkaldy's time, and he must have been well acquainted with the fact that it is easier to break nicked bars cut transverse to, rather than in the direction of, the fiber of both wrought iron and steel. He had, however, no means for measuring the effect of fiber upon the energy required to break such pieces.

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[2] "We cannot insist that, as regards the ultimate particles, this difference is chiefly in strength rather than in ductility or flexibility; but as regards the mass as a whole it may be treated as a difference in strength." (Howe)

[3] "Experiments on Wrought Iron and Steel," Glasgow, 1862.

[4] This conclusion is somewhat remarkable, but merits no discussion here.

Charpy[5] and Brearley[6] (see also Allcut and Miller)[7] seem to have been the first to report on the effect of fiber on the notch toughness of steel. Of Charpy's experiments, one series was conducted on samples cut from medium carbon, basic open-hearth steel (phosphorus, 0.05 per cent; sulphur, 0.06 per cent). These samples were taken transversely and longitudinally; (1) from an ingot 355 x 355 millimeters square; (2) from a portion of this ingot which had been forged to 225 x 225 millimeters square—a reduction of area of about 60 per cent; and (3) from another portion of the same ingot which had been forged to 125 x 125 millimeters square—a reduction of area of about 88 per cent. Before test pieces were machined from these samples, they were quenched from 1560 degrees Fahr. (850 degrees Cent.), and tempered at 1200 degrees Fahr. (650 degrees Cent.) for the implied purpose of bringing them in all cases into structural conditions as closely similar as possible. The results of the tensile and impact tests made on the pieces cut from the samples are shown in Table I.

Table I

Percentage Reduction in Area by Forging	Tensile Strength (p.s.i.)	Percentage Elongation (gauge length unknown)	Reduction of Area (Per Cent)	Charpy Impact Number (kg-m.)
		Longitudinal		
nil	101,400	16	33	3.3
60	99,700	18	33	3.5
88	103,400	23	61	9.1
		Transverse		
nil	101,800	14	22	3.4
60	100,600	11	27	2.0
88	97,300	4	8	1.5

Another series of tests was made by Charpy on the same steel, but forged to a section 75 x 75 millimeters square, corresponding to a reduction of area of about 95.5 per cent. Only notched-bar test pieces were taken from this forging, "but in lieu of longitudinal and transverse bars, two others were taken at angles of 20 and 45 degrees with the axis, all taken from the same longitudinal cut." The impact

[5]Charpy, *Journal*, Iron and Steel Institute, Vol. 98, 1918, p. 7-25.

[6]Brearley, Brown Bayley's Journal.

[7]Allcut and Miller, "Materials and Their Application to Engineering Design," C. Griffin and Co., Ltd., London, 1923.

tests carried out after quenching and tempering the bars gave the results shown in Table II.

Table II

Angle of Notch Relative to Direction of Rolling (Degrees)	Charpy Impact Number (kg-m.)
0	1.3
20	1.5
45	3.4
90	13.5

The results of Brearley's investigations, which were carried out on Bessemer steel containing 0.23 per cent carbon, 0.97 per cent manganese, and 3.08 per cent nickel, are shown in Fig. 1, taken from Allcut and Miller's book.

Work on this subject has been carried out by many other investigators[8] and the general conclusions reached in regard to the tensile properties of ferrous materials are essentially at one with those arrived at by Kirkaldy seventy-six years ago.

There is no doubt that the difference between the transverse and longitudinal properties can be reduced to a minimum in clean steel by careful forging and suitable heat treatment, but in most commercial steels the ratio of the values for transverse and longitudinal impact tests will almost invariably be high, being dependent largely on the number and nature of the inclusions present in the material under test. According to Brearley[9] "the ratio between the average longitudinal and transverse impact figures" is "a very good indication of the comparative freedom of steel from slag occlusions, etc., and" is "incidentally a good index of the care taken in the melting and casting operations."

Description of Present Experiments

In this connection it is of interest to speculate as to the effect of cooling rate and actual grain size upon the notch toughness of a given steel in directions transverse and parallel to the direction of rolling. Will they, or will they not, have an important influence upon this property?

[8]Roš, Eidgenössische Materialprüfungsanstalt an der E.T.H. Zurich, Rep. 52, 1930, p. 34.

[9]Brearley, *Journal*, Iron and Steel Institute, 1918, Vol. 98, p. 34.

In an attempt to answer this question, a series of 112 pieces was cut from a steel flat, 5.5 inches wide and ½ inch thick, of the following chemical analysis:

	Per Cent
Carbon	0.09
Silicon	0.51
Manganese	0.47
Sulphur	0.016
Phosphorus	0.015

This material was picked at random from the stock of a local dealer.

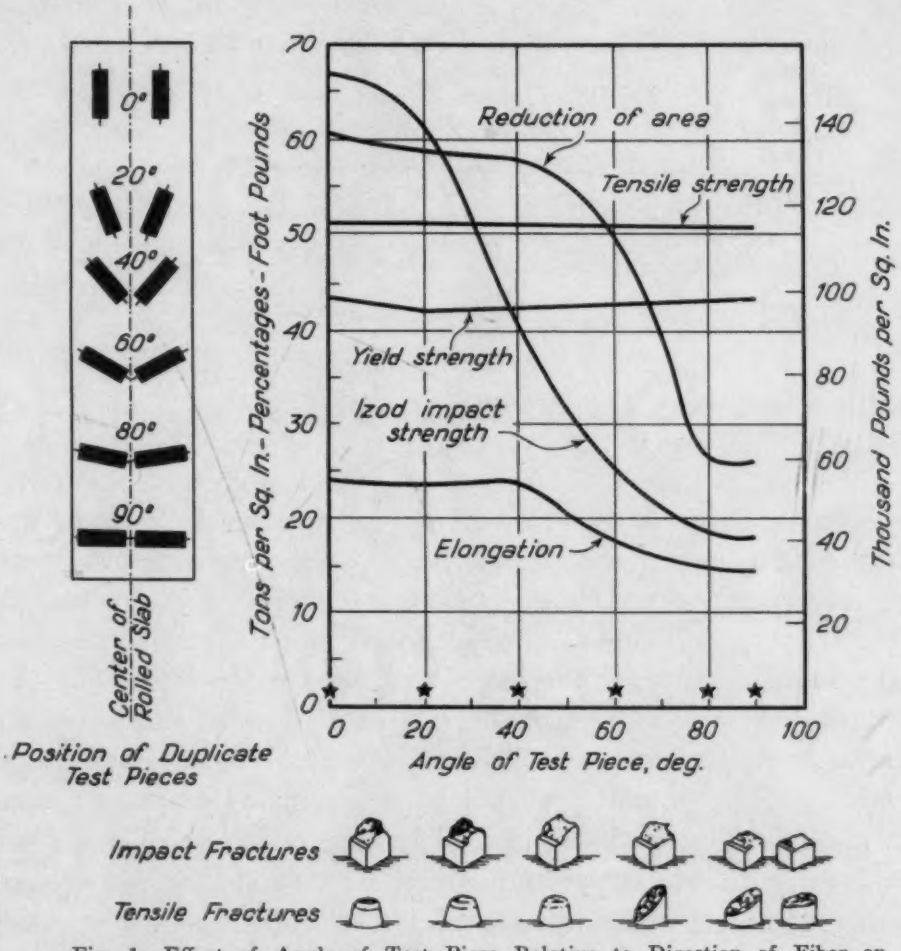


Fig. 1—Effect of Angle of Test Piece Relative to Direction of Fiber on Mechanical Properties of Steel (Brearley).

The individual pieces were approximately 5.5 inches long, ½ inch wide, and ½ inch thick. They were cut from the flat in groups of eight, one group being cut transverse to the length of the flat, the next group parallel to it, and so on. The pieces were, of course, marked so as to denote their original directions relative to the length

of the flat. However, no other attempt was made to distinguish the pieces after they had been cut, so that it would have been impossible, had it been necessary to do so later, to account for variations in the composition of the steel in the flat. The individual pieces were carefully machined on all sides until they were approximately 0.4 x 0.4 inch square. They were then ground accurately to 0.395 x 0.395 inch square.

Jackets, as shown in Fig. 2, had been prepared to receive the pieces. These jackets were of the following outside dimensions:

Large	7⅜ inches long x	1¼ inches wide x	1¼ inches deep
Medium	7⅜ inches long x	1 inch wide x	1 inch deep
Small	7⅜ inches long x	¾ inch wide x	¾ inch deep

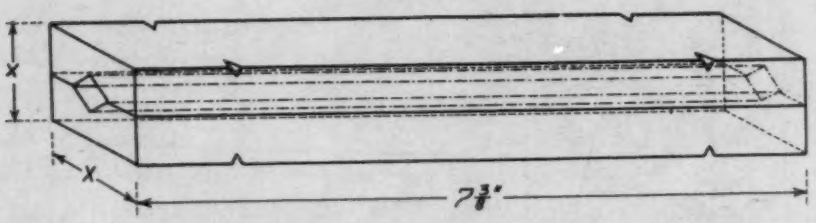


Fig. 2—Appearance and Dimensions of Jackets Used to Control Time of Cooling of Samples.

Rectangular grooves (Fig. 2) were shaped in the jackets, which before final grinding were calorized to ensure their permanence at high temperatures. After the jackets had been calorized, heated to bright redness, and cooled slowly, the grooves in them were given a final grinding so as to fit the pieces as snugly as possible. The object of the jackets was to control the rate of cooling of the pieces after removal from the furnace in which they were heated to different temperatures. The pieces were placed individually in jackets, which were then tightly wired together. The open ends of the jackets were now filled with fire clay, after which they (with the pieces snugly encased in them) were introduced into the furnace. The rate of cooling of individual pieces varied rather widely in the case of those fitted with large jackets—the time of cooling from 1550 degrees Fahr. (840 degrees Cent.) to 950 degrees Fahr. (510 degrees Cent.), for example, varied from 475 to 675 seconds. This was due mainly to the fact that the conditions of cooling in this jacket were such as to cause large variations in the time of cooling of the pieces at the A1 point. The times of cooling over the same range (1550 to 950 de-

grees Fahr.— 840 to 510 degrees Cent.) in the other jackets were as follows:

Medium	308 ± 5 seconds
Small	305 ± 5 seconds

When cooling in air, unjacketed, the temperature of the pieces fell from 1550 to 950 degrees Fahr. (840 to 510 degrees Cent.) in close to 110 seconds. No attempt was made to determine the time of cooling over the above temperature range of the unjacketed pieces quenched in oil (Houghton's No. 2 soluble oil) at 20 degrees Fahr.; the average rate of cooling from 1470 to 1290 degrees Fahr. (700 to 600 degrees Cent.) was measured, however, and found to be 80.0 degrees Fahr. per second. This compares with rates over the same range of 1.1, 1.7, 1.9, and 6.7 degrees Fahr. per second for the samples cooled in the large, medium, and small jackets, and unjacketed, respectively.

The upper critical point on heating (Ac3) of this steel was found to be in the close neighborhood of 1545 degrees Fahr. (840 degrees Cent.), and the following temperatures were chosen as those to which to heat, and from which to cool, the pieces in one or other of the ways described above:

1570 Degrees Fahr. (853 Degrees Cent.)
1595 Degrees Fahr. (868 Degrees Cent.)
1620 Degrees Fahr. (882 Degrees Cent.)
1645 Degrees Fahr. (896 Degrees Cent.)
1670 Degrees Fahr. (909 Degrees Cent.)
1695 Degrees Fahr. (923 Degrees Cent.)
1720 Degrees Fahr. (937 Degrees Cent.)

Heating of the pieces, with or without jackets, was carried out in a gas furnace, the temperature of which could be closely controlled. The temperature of individual pieces was estimated by introducing into the furnace, together with them, pilot samples into which thermocouples were fitted. The temperatures of the pilot samples were traced on the chart of a recording potentiometer. It was assumed that the temperatures of the pieces were at all times very close to, if not identical with, those of the pilot samples. The pieces were raised to and held at one or other of the above temperatures for ½ hour, after which they were either cooled in still air or quenched, as desired.

After being treated, the pieces were ground to 0.3937 ± 0.0010 inch × 0.3937 ± 0.0010 inch square (10 mm. × 10 mm. square). Notches were cut in them in the positions shown in Fig. 3, which is

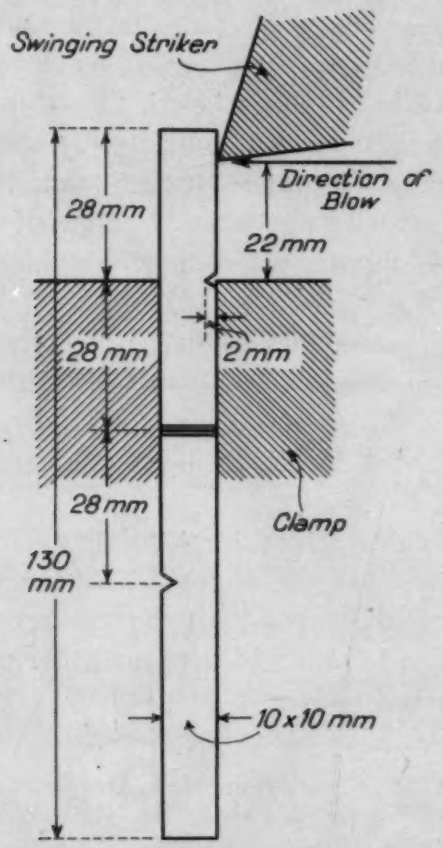


Fig. 3—British Standard Izod Test Piece (Batson and Hyde).

a sketch of the British standard cantilever-type 3-notch test piece for use in the Izod test. The notch in this test piece has an angle of 45 degrees, is 2 millimeters deep, and has a root radius of 0.25 millimeters. Except that in every case the pieces exceeded 130 millimeters in length, their dimensions agreed with those shown in Fig. 3.

The results of the impact tests on these pieces are given in Tables III and IV, the first of which deals with the tests on the transverse samples, the second with those on the longitudinal samples.

Front views of the fractures of four of these pieces are shown in Fig. 4. That to the left of the picture is of one of the longitudinal pieces which had been cooled in air, the next is of one of the

longitudinal pieces which had been quenched in oil, the next is of one of the transverse pieces which had been cooled in air, while the last is of one of the transverse pieces which had been quenched in oil. There is little to choose between the fractures of the air-cooled and

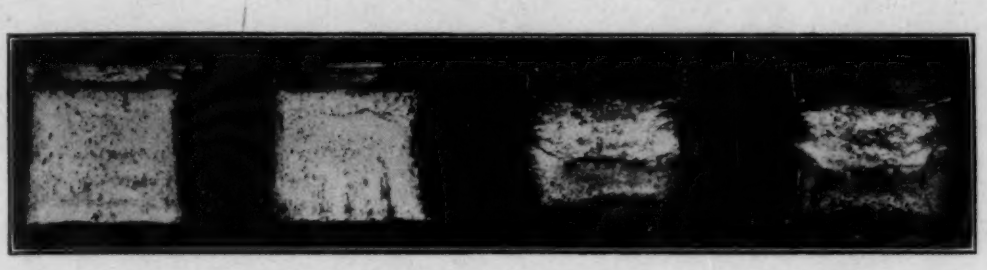


Fig. 4—Front Views of Fractures of Izod Test Pieces—Left, Longitudinal; Right, Transverse.

quenched pieces, whether longitudinal or transverse, but a marked difference exists between the fractures of the longitudinal and transverse pieces, whether air-cooled or quenched. None of the fractures can be termed "brittle"; the longitudinal fractures, however, show less

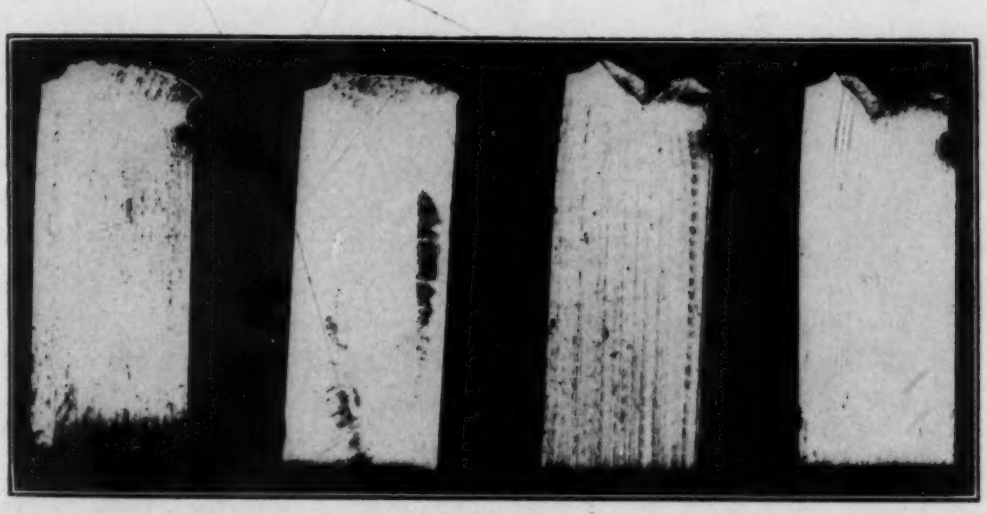


Fig. 5—Side Views of Fractures of Izod Test Pieces—Left, Longitudinal; Right, Transverse.

evidence of ductility than do the transverse. This is probably due, in part, to their manner of deformation.

The side views of the same fractures are shown in the same order in Fig. 5. It is noteworthy that the position of the notch relative to the axis of the piece had little effect, if any, upon the appearance of the fractures of the longitudinal pieces, whereas this factor was of some, though slight, importance in determining the

appearance of the transverse fractures.[10] The notches in the transverse pieces shown in Figs. 4 and 5 were at right angles to the direction of rolling of the flat.

After the impact tests had been done, Vickers hardness tests were made on the longest portions of the broken pieces. Three impressions were made on each portion, and these agreed well among themselves. The numbers corresponding to these impressions are quoted as Brinell hardness numbers in Tables III and IV. Finally, tiny tensile test samples were cut from the longest portions of the broken pieces, and tested in a tensometer machine. The results of these tests are also quoted in Tables III and IV.

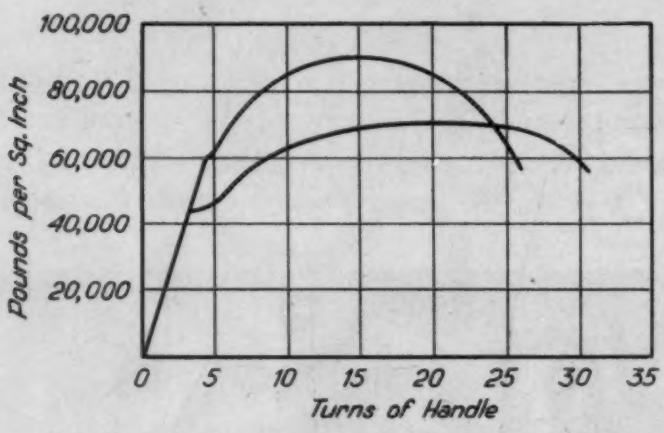


Fig. 6—Tensometer Autographic Stress-Strain Diagrams for Longitudinal and Transverse Tensile Test Pieces.

The effect of quenching on the form of the stress-strain diagram for this steel (longitudinal pieces air-cooled and quenched from 1570 degrees Fahr. (850 degrees Cent.) respectively) is quite marked. It is nicely shown in Fig. 6, which is a reproduction of two of the autographic diagrams obtained on the tensometer, superimposed one on the other. The stress values in Fig. 6 should be multiplied by 1.07 to give the correct figure. The "turns of handle" are a rough measure of strain. The diagrams serve a useful purpose, but cannot be considered as accurate graphical representations of the results of the tests.

Microscopic examination was made of longitudinal sections of all the transverse pieces and of transverse sections of all the longitudinal pieces. None of the samples showed banding that could be con-

[10] It did not noticeably influence the impact values.

Table III

Sample Number	Time of Cooling from 1550 to 950° F. (sec.)	Temp. of Heating (°F.)	Brinell Hardness Number	Yield Strength (p.s.i.)	Tensile Strength (p.s.i.)	Elongation (% on 1 in.)	Reduction of Area (%)	Average Izod Impact Value (ft-lb.)
A-1	...	....	136	39,000	72,000	40	58	30
+A-2	475-675	1570	132	45,000	73,000	40	59½	40
+A-3	380	1570	132	49,500	76,000	40	57	44
+A-4	305	1570	134	47,000	73,000	40	57½	39
+A-5	110	1570	141	50,500	77,000	37	56	39
A-2/5 (avg.)	Air-cooled	1570	135	48,000	74,750	39¼	57½	40½
+A-6	Quenched	1570	214	.....	103,500	34	55½	33
A-7	475-675	1595	120	48,000	75,000	35	57	35
A-8	380	1595	120	47,000	73,000	37	57	39
A-9	305	1595	136	43,000	70,000	40	59	38
A-10	110	1595	143	45,000	69,000	30	59	40
A-7/10 (avg.)	Air-cooled	1595	130	45,750	71,750	35½	58	38
A-11	Quenched	1595	202	.....	101,000	30	54	28
+A-12	475-675	1620	134	47,500	75,000	37½	57	39
+A-13	380	1620	148	45,000	73,500	40	55	37
+A-14	305	1620	136	45,000	74,000	40	57½	38
+A-15	110	1620	144	48,500	76,500	36½	59	38
A-12/15 (avg.)	Air-cooled	1620	141	46,500	74,750	38½	57	38
+A-16	Quenched	1620	202	.....	99,000	25	55½	25
A-17	475-675	1645	123	42,000	72,000	40	59	33
A-18	380	1645	131	46,000	74,000	40	61	38
A-19	305	1645	127	45,000	74,000	40	59	40
A-20	110	1645	130	45,000	76,000	37	57	36
A-17/20 (avg.)	Air-cooled	1645	128	44,500	74,000	39¼	59	36¾
A-21	Quenched	1645	190	.....	88,000	30	59	29
+A-22	475-675	1670	138	45,000	74,500	40	57	36
+A-23	380	1670	142	44,000	74,000	40	59	36
+A-24	305	1670	136	43,500	75,500	37½	59½	36
+A-25	110	1670	141	44,500	75,500	37½	58½	33
A-22/25 (avg.)	Air-cooled	1670	139	44,250	74,875	38¾	58½	35¼
+A-26	Quenched	1670	191	.....	93,000	27½	59½	33
A-27	475-675	1695	142	45,000	72,000	40	65	35
A-28	380	1695	154	44,000	73,000	40	57	39
A-29	305	1695	127	42,000	74,000	40	59	36
A-30	110	1695	132	45,000	75,000	45	59	36
A-27/30 (avg.)	Air-cooled	1695	139	44,000	73,500	41¼	60	36½
A-31	Quenched	1695	218	.....	111,000	20	49	26
+A-32	475-675	1720	138	40,500	71,500	37½	56	35
+A-33	380	1720	141	40,000	72,500	35	59	34
+A-34	305	1720	136	39,000	73,000	38½	60	34
+A-35	110	1720	137	42,000	75,000	36	61½	36
A-32/35 (avg.)	Air-cooled	1720	138	40,250	73,000	36¾	59	34¾
+A-36	Quenched	1720	206	.....	105,500	22½	53	25

(+—Results are means of duplicate tests.)

sidered as likely to influence seriously the transverse mechanical properties of the steel. Banding was most marked in pieces A-2 and B-2, which had been heated to 1570 degrees Fahr. (853 degrees

Table IV

Sample Number	Time of Cooling from 1550 to 950° F. (sec.)	Temp. of Heating (°F.)	Brinell Hardness Number	Yield Strength (p.s.i.)	Tensile Strength (p.s.i.)	Elongation (% on 1 in.)	Reduction of Area (%)	Average Izod Impact Value (ft-lb.)
B-1	...	....	150	42,000	74,000	40	60	52
+B-2	475-675	1570	139	46,000	73,000	42½	65½	90
+B-3	380	1570	146	46,500	76,500	37½	66½	87
+B-4	305	1570	150	48,500	73,500	40	68	91
+B-5	110	1570	153	48,000	79,000	40	67½	90
B-2/5 (avg.)	Air-cooled	1570	147	47,250	75,500	40	67	89½
+B-6	Quenched	1570	203	63,000‡	100,000	32½	70	111
B-7	475-675	1595	143	47,000	76,000	40	62	86
B-8	380	1595	135	48,000	77,000	40	65	89
B-9	305	1595	145	50,000	78,000	40	65	90
B-10	110	1595	155	53,000	78,000	37	66	95
B-7/10 (avg.)	Air-cooled	1595	145	49,500	77,250	39¼	64½	90
B-11	Quenched	1595	201	.....	103,000	35	69	112
+B-12	475-675	1620	138	49,000	77,500	42½	63½	81
+B-13	380	1620	150	50,500	77,000	40	65	85
+B-14	305	1620	139	46,500	73,000	40	66½	89
+B-15	110	1620	145	50,000	80,500	40	65	86
B-12/15 (avg.)	Air-cooled	1620	143	49,000	77,000	40½	65	85¼
+B-16	Quenched	1620	195	67,500‡	100,500	32½	69	102
B-17	475-675	1645	127	51,000	80,000	40	62	85
B-18	380	1645	132	47,000	74,000	45	66	93
B-19	305	1645	146	47,000	76,000	40	65	91
B-20	110	1645	148	51,000	80,000	40	65	90
B-17/20 (avg.)	Air-cooled	1645	138	49,000	77,500	41¼	64½	89¾
B-21	Quenched	1645	196	.....	106,000	29	60	104
+B-22	475-675	1670	140	44,000	73,500	45	63½	89
+B-23	380	1670	157	45,000	74,000	41½	65½	86
+B-24	305	1670	142	45,500	75,500	40	63½	89
+B-25	110	1670	147	47,000	77,500	40	67	86
B-22/25 (avg.)	Air-cooled	1670	147	45,375	75,125	41½	65	87½
+B-26	Quenched	1670	192	.....	99,000	35	69½	98
B-27	475-675	1695	140	43,000	70,000	45	65	90
B-28	380	1695	135	46,000	79,000	45	65	78
B-29	305	1695	138	46,000	77,000	40	65	86
B-30	110	1695	149	43,000	74,000	45	69	85
B-27/30 (avg.)	Air-cooled	1695	141	44,500	75,000	43¾	66	84¾
B-31	Quenched	1695	205	.....	126,000	20	54	88
+B-32	475-675	1720	138	47,500	78,500	42½	63½	82
+B-33	380	1720	144	48,000	78,000	40	63½	77
+B-34	305	1720	144	40,000‡	74,500	35	65½	80
+B-35	110	1720	147	45,000	80,500	40	65½	72
B-32/35 (avg.)	Air-cooled	1720	143	45,125	77,875	39½	64½	77¾
+B-36	Quenched	1720	202	.....	96,000	32½	74½	107

(+—Results are means of duplicate tests.)
(‡—One sample showed no yield; the other, the yield strength quoted.)

Cent.) and cooled from 1550 to 950 degrees Fahr. (842 to 510 degrees Cent.) in from 475 to 675 seconds. Fig. 7 is a photomicrograph typical of the structure of these pieces. Fig. 8 is representa-

tive of the structures of A-4 and B-4 heated to 1570 degrees Fahr. (855 degrees Cent.) and cooled from 1550 to 950 degrees Fahr. (840 to 510 degrees Cent.) in 305 seconds; Fig. 9 is typical of the structures of A-5 and B-5 cooled from 1570 degrees Fahr. (855 degrees Cent.) through the above temperature range in 110 seconds; and Fig. 10 is typical of the structure of the piece quenched from 1570 degrees Fahr. (855 degrees Cent.). Figs. 11 to 15 and 16 to 20 show structures representative of those formed in the pieces heated to 1595 and 1720 degrees Fahr. (870 and 935 degrees Cent.), respectively, and cooled at the five different rates.

Apart from pieces A-2 and B-2 (which, as can be seen in Fig. 7, showed but slight banding), the pieces most slowly cooled from 1595 and 1620 degrees Fahr. (868 and 880 degrees Cent.), respectively (pieces A-7, B-7, A-12, and B-12), alone showed any evidence whatsoever of this type of structure.

Discussion of Results of Present Experiments

The first conclusion reached from an examination of the results quoted in Tables III and IV is that in the particular case now under consideration, variations in the rate of cooling in air from temperatures ranging from 1570 to 1720 degrees Fahr. (855 to 940 degrees Cent.) are unimportant in their effect on the mechanical properties. Hence, in these tables the average values for the mechanical properties of the pieces cooled in air from various temperatures have been calculated and placed alongside those for the mechanical properties of the quenched pieces. This arrangement enables a more rapid assessment to be made of the results as a whole.

The second conclusion is that the temperature of heating does not markedly influence the mechanical properties of this particular steel, in either the air-cooled or the quenched state, until it exceeds about 1670 degrees Fahr. (910 degrees Cent.).

The third, and, of course, not unexpected, conclusion is that quenching increases the yield and tensile strengths of this steel over those of the material in the air-cooled state.

The fourth and most surprising conclusion is that, whereas quenching this material lowers its notch toughness (on the average by about 23 per cent) below that of the air-cooled material when tested transversely, it quite appreciably raises the notch toughness

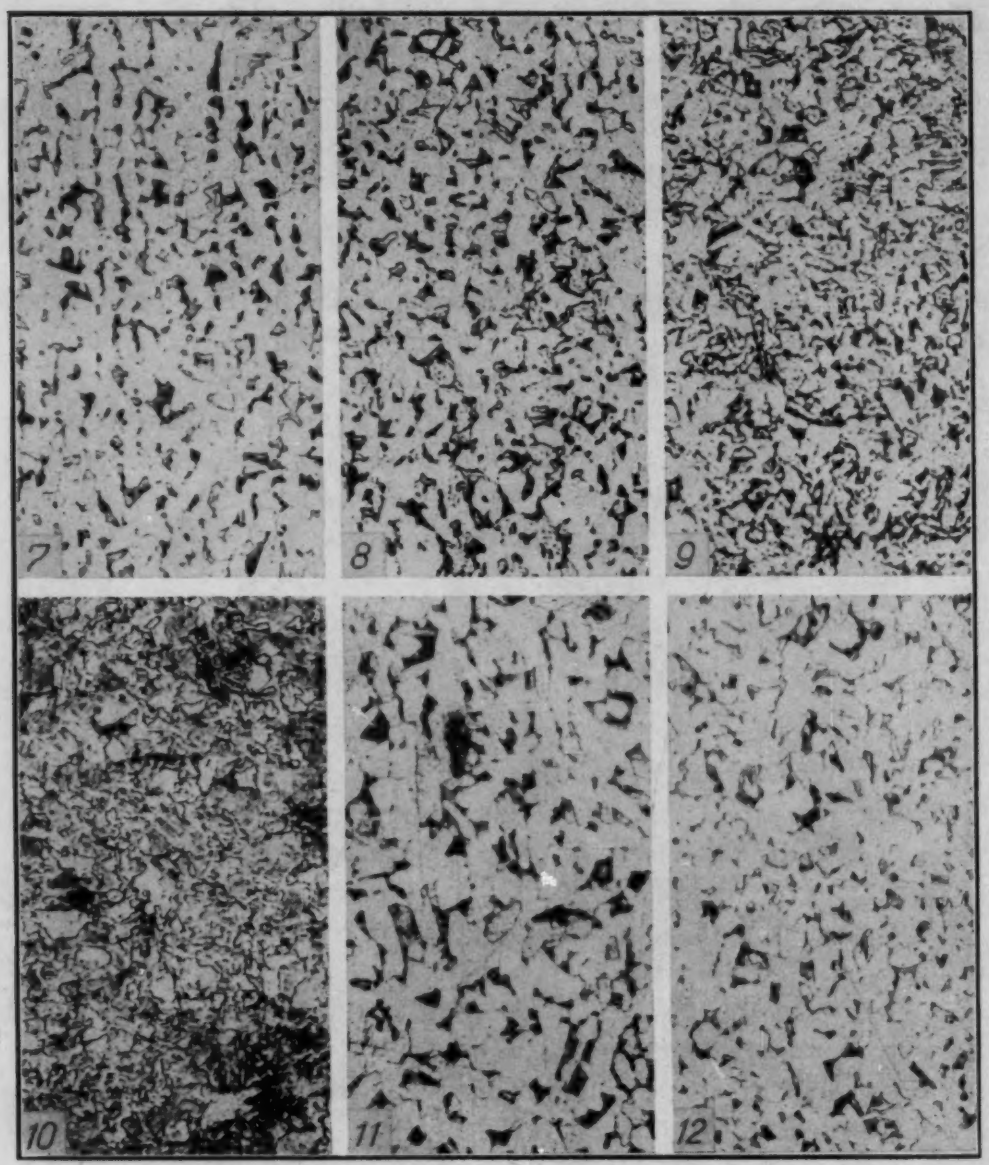


Fig. 7—Structure of Samples as Received. × 100.
Fig. 8—Structure of Samples Heated to 1570 Degrees Fahr. (855 Degrees Cent.) and Cooled in 305 Seconds. × 100.
Fig. 9—Structure of Samples Heated to 1570 Degrees Fahr. (855 Degrees Cent.) and Cooled in 110 Seconds. × 100.
Fig. 10—Structure of Samples Quenched in Oil from 1570 Degrees Fahr. (855 Degrees Cent.). × 100.
Fig. 11—Structure of Samples Heated to 1595 Degrees Fahr. (870 Degrees Cent.) and Cooled in 475-675 Seconds. × 100.
Fig. 12—Structure of Samples Heated to 1595 Degrees Fahr. (869 Degrees Cent.) and Cooled in 380 Seconds. × 100.

(on the average by about 14 per cent) above that of the air-cooled material when tested longitudinally. In other words, the longitudinal notch sensitivity of this steel is decreased by quenching, whereas its

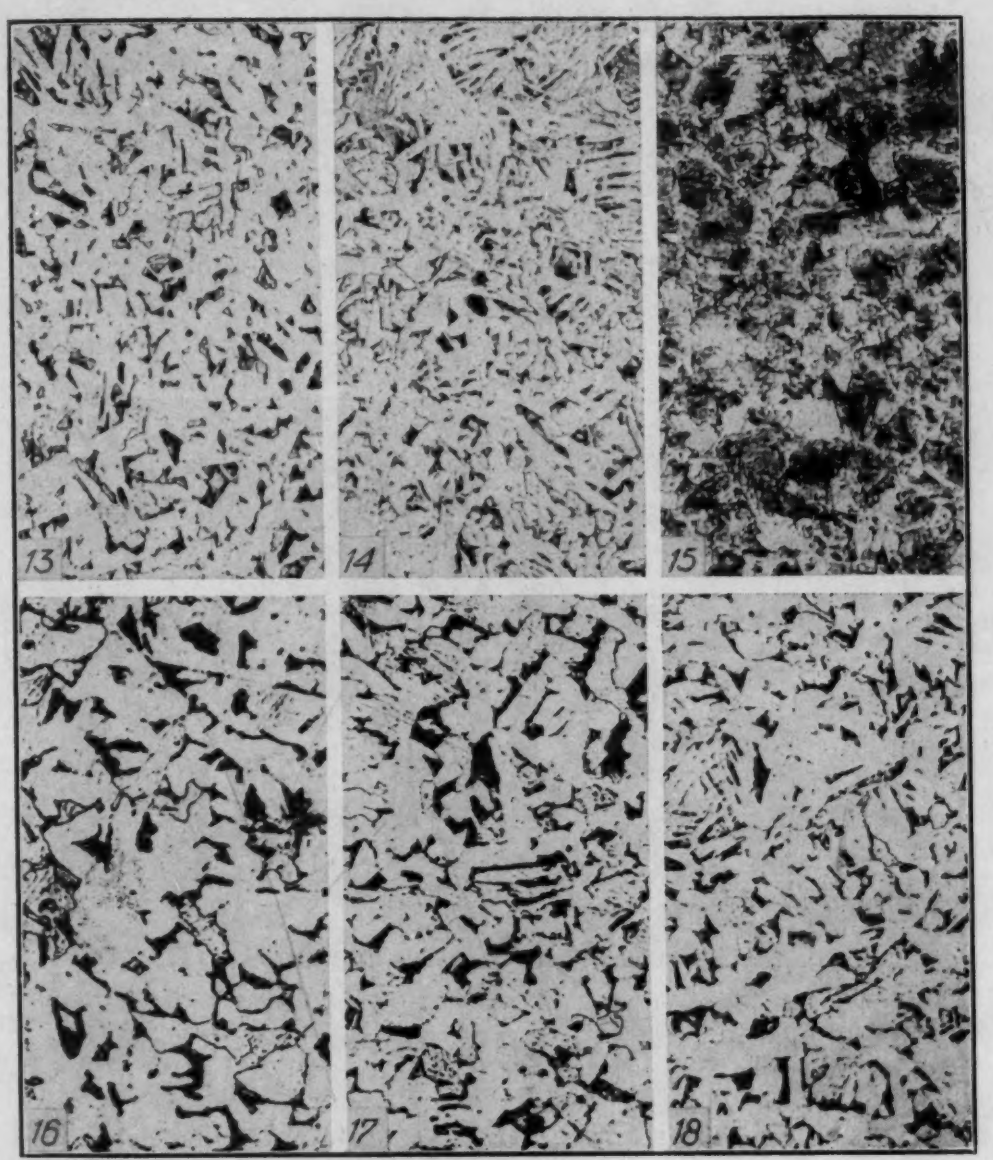


Fig. 13—Structure of Samples Heated to 1595 Degrees Fahr. (870 Degrees Cent.) and Cooled in 305 Seconds. × 100.
Fig. 14—Structure of Samples Heated to 1595 Degrees Fahr. (870 Degrees Cent.) and Cooled in 110 Seconds. × 100.
Fig. 15—Structure of Samples Heated to 1595 Degrees Fahr. (870 Degrees Cent.) and Quenched in Oil. × 100.
Fig. 16—Structure of Samples Heated to 1720 Degrees Fahr. (935 Degrees Cent.) and Cooled in 475-675 Seconds. × 100.
Fig. 17—Structure of Samples Heated to 1720 Degrees Fahr. (935 Degrees Cent.) and Cooled in 380 Seconds. × 100.
Fig. 18—Structure of Samples Heated to 1720 Degrees Fahr. (935 Degrees Cent.) and Cooled in 305 Seconds. × 100.

transverse notch sensitivity is by the same means increased. To the ductility of this steel, as measured in terms of percentage elongation and percentage reduction of area, the same remarks rather generally apply.

In the present state of our knowledge of the mechanism of the impact test it is by no means easy to give reasons for these interesting results. The following suggestions, which are not to be looked upon as the final opinions of the authors on what is so obviously a matter for more experiment, are put forward mainly for the sake of promoting discussion.

If it be assumed that the behavior of the longitudinal pieces of this steel represents with reasonable accuracy that of homogeneous, non-isotropic steel of the same type, it would appear that quenching

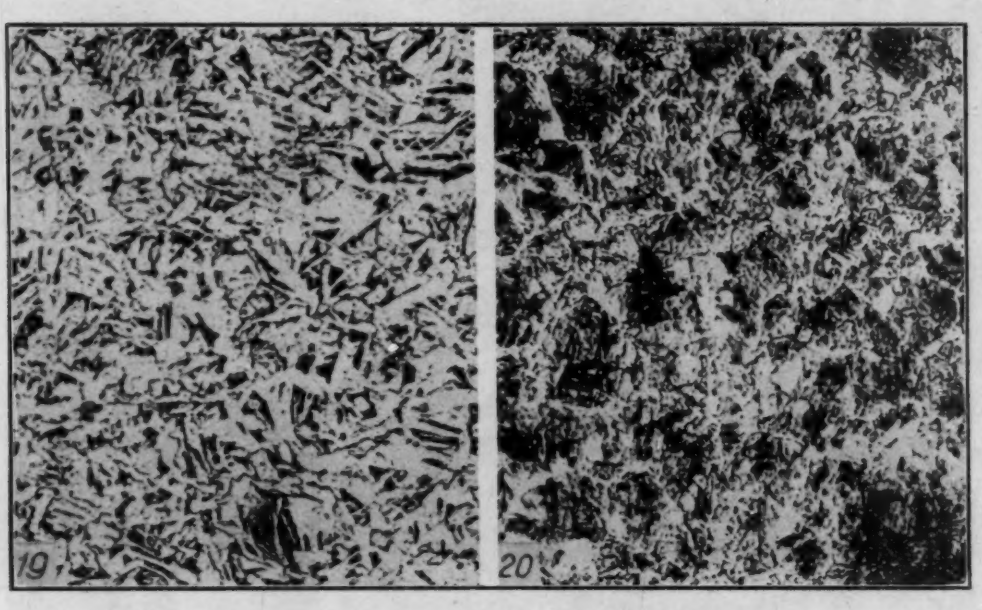


Fig. 19—Structure of Samples Heated to 1720 Degrees Fahr. (935 Degrees Cent.) and Cooled in 110 Seconds. × 100.
Fig. 20—Structure of Samples Heated to 1720 Degrees Fahr. (935 Degrees Cent.) and Quenched in Oil. × 100.

increases the cleavage strength of homogeneous, non-isotropic material to a proportionately greater amount than its resistance to plastic flow.

The fact that the fractures of the longitudinal pieces, both air-cooled and quenched, are so similar in shape would seem to indicate that during test the total deformation of this steel is much the same in both states. From this it might be inferred that the energy absorbed in deforming quenched, homogeneous, non-isotropic steel of this type would be little, if any, different from that absorbed in deforming the air-cooled material. Hence, the reduction in the notch-sensitivity of steel of this type brought about by quenching must be due largely, if not entirely, to an increase in its cleavage strength.

Turning now to a consideration of the transverse pieces, in view of the above it may be assumed that the cleavage strength per se of this steel can be increased by quenching to the point where its Izod impact number is about 23 per cent more than that of the air-cooled steel. Now, the fractures of the transverse pieces, both air-cooled and quenched, are so similar in shape as to suggest that the amount of plastic flow of this steel is not much affected by heat treatment, other things being the same. Hence, the effect of fiber in this steel must be to reduce very materially its resistance to plastic flow; it does not appear as though it is important in its effect upon the cleavage strength of the material. Whether this would be true of the effect of fiber in all steels remains yet to be proved.

EFFECTS OF COLUMBIUM AND OTHER ADDITION AGENTS ON LOW CHROMIUM STEELS

By Russell Franks

Abstract

In fabricating and using the wrought 4-6 per cent chromium steels for resisting mild corrosion and deterioration at temperatures between 400 and 650 degrees Cent. some difficulty due to the development of low toughness has been encountered. The difficulty met with during fabrication is undoubtedly due to the air hardening properties of the steels. The trouble arising in service has occurred in annealed steels and is especially noticeable after the equipment has operated for long periods and is shut down for repairs during the winter months when the temperature is low. It has also been claimed that the development of low toughness in service is connected with temper brittleness which is measured by heating the steels to a temperature slightly above the Ac_1 change point and tempering at 650 degrees Cent., followed by rapid and slow cooling, the Greaves-Jones test. Susceptibility to this type of brittleness is represented by the ratio of the impact value of the sample rapidly cooled to that of the sample slowly cooled from the tempering temperature.

A large number of tests were made to find an improved low chromium steel free of air hardening, which would retain its toughness after exposure under the conditions of the Greaves-Jones test. The results showed that the addition of columbium gave non-hardenable 4-6 per cent chromium steels with a high degree of toughness. Molybdenum was found to improve the creep strength of the steels containing columbium and should be employed when this is an important factor. Columbium additions to low carbon 3-4 and 2-3 per cent chromium steels proved to be beneficial, indicating that this element should markedly enhance the utility of all these low chromium steels.

STEELS of relatively low chromium content have been used during the past few years for resisting mild corrosion both at normal

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and moderately elevated temperatures. Among the steels that have received considerable attention are those containing between 4 and 6 per cent chromium. Steels of this type have been applied in the form of cracking tubes, tube sheets, transfer lines, valves, baffles, etc., in the oil refining industry. They have also been used in superheaters operating at moderately high temperatures and as furnace parts that function under similar conditions.

While the steels have rendered good service in most instances, difficulty has been encountered because of low toughness, which may develop during fabrication or in subsequent service. The low toughness that develops during fabrication is unquestionably related to air hardening. The steels also become relatively hard when they are heated at the temperatures necessary for hot forming or welding and are then allowed to cool rapidly. The embrittlement observed at normal and subnormal temperatures in annealed steels that have been exposed in service for long periods at temperatures between about 400 and 650 degrees Cent. (750 and 1200 degrees Fahr.) is of a different type. Observations by Dixon and Wilten[1] have led them to state that this type of embrittlement occurs without an increase in hardness or tensile strength. They also state that in some instances correlation has been found between this type of brittleness and temper brittleness, that according to Greaves and Jones[2] is produced after hardening by slow cooling from temperatures in the vicinity of 650 degrees Cent. (1200 degrees Fahr.). In fact, Wilten[3] shows that the 4-6 per cent chromium steels are subject to temper brittleness and failure may occur in oil refinery service because of loss of toughness. He states that if molybdenum is added the steels are not subject to temper brittleness, and experience has shown that they function more satisfactorily.

The carbon content has a marked influence on susceptibility to these three types of brittleness, and while data have been published on steels containing 0.15-0.20 per cent carbon little information is available on 4-6 per cent chromium steels containing 0.10 per cent or less carbon. It was decided to investigate the lower carbon steels, and the nonhardenable chromium steels containing titanium and

[1]H. M. Wilten and E. S. Dixon, "Aging Embrittlement of 4 to 6 Per Cent Chromium Steel," *Proceedings*, American Society for Testing Materials, Vol. 34, p. 59, 1934.

[2]R. H. Greaves and J. A. Jones, "Temper Brittleness of Steel; Susceptibility to Temper Brittleness in Relation to Chemical Composition," *Journal*, Iron and Steel Institute, Vol. CXI, p. 231, 1925.

[3]H. M. Wilten, "Correlation of Failures from Embrittlement of 4-6 per cent Chromium Steel with the Notched Bar Impact Test," *Proceedings*, American Society for Testing Materials, Chicago Meeting, Sept. 30 to Oct. 4, 1935.

columbium[4] to see whether they would retain their toughness after rapid cooling from 900 degrees Cent. (1650 degrees Fahr.) and subsequent holding within the range between 400 and 650 degrees Cent. (750 and 1200 degrees Fahr.), and also after annealing and holding within the same range of temperature. It was further decided to determine whether the steels were subject to temper brittleness. Difficulties have been met with because of the ill effects of subnormal temperatures on the toughness of steels of this type, and it was felt that if a modified 4-6 per cent chromium steel with a high degree of toughness at all temperatures extending from subnormal temperatures up to about 900 degrees Cent. (1650 degrees Fahr.) could be found, the material could be applied with greater facility than the present day steels of this type.

With this purpose in view work was done on low carbon 4-6 per cent chromium steels with normal silicon and manganese contents. In some instances these represented commercial steels, while in others they were made under experimental conditions that involved ingots varying in size from 2 by 2 by 16 inches to 8 by 8 by 36 inches. These ingots were hot-worked into ¾-inch diameter bars and ½-inch plates from which standard Izod impact samples were taken and investigated under conditions to be later described. Samples in each instance were tested for hardness, but all the Brinell values will not be given as it would involve submitting considerable unnecessary data. In conducting the impact tests at low temperatures the various samples were held at temperature for at least ½ hour, after which they were quickly transferred to the impact machine and tested within 5 seconds.

The investigation was started on the low carbon 4 to 6 per cent chromium steels with or without molybdenum described in Fig. 1, which shows the results of temper brittleness tests on samples quenched from 900 degrees Cent. (1650 degrees Fahr.) and tempered for different periods between ½ and 12 hours at 650 degrees Cent. (1200 degrees Fahr.), followed by furnace cooling. The steels were quenched from 900 degrees Cent. (1650 degrees Fahr.) because this temperature represents a point slightly above the Ac_1 change. The tests showed that when the tempering period at 650 degrees Cent. (1200 degrees Fahr.) was increased to 2 hours the

[4]F. M. Becket and Russell Franks, "Titanium and Columbium in Plain High Chromium Steels," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 113, 1933.

steels reached optimum toughness and remained in this condition after tempering for 4, 8 and 12 hours followed by furnace cooling. Although the data are not given, similar results were secured after air cooling from 650 degrees Cent. (1200 degrees Fahr.) indicating that if the carbon content was kept low the steels were not noticeably susceptible to the development of brittleness under the conditions of the test.

In the next experiments on the same steels and a similar steel containing tungsten, samples were respectively water-quenched and

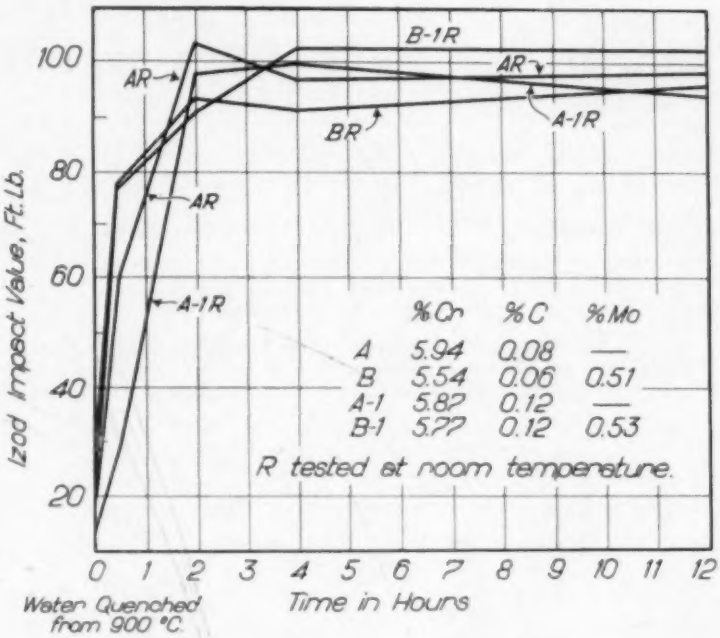


Fig. 1—Effect of Tempering for Different Periods at 650 Degrees Cent. on the Toughness of 4 to 6 Per Cent Chromium Steels with and Without Molybdenum.

air-cooled from 900 degrees Cent. (1650 degrees Fahr.) and held at 400, 450, 550, 650 and 750 degrees Cent. (750, 840, 1020, 1200 and 1380 degrees Fahr.) for two hours and furnace-cooled. It was decided to test samples so treated at room temperature, and also at —40 degrees Cent. to approximate the most severe condition that might exist during the winter months. As shown in Figs. 2 and 3, the steels have low toughness in the quenched and air-cooled conditions. This is due to the fact that the Brinell hardness number for the steels varied between 387 and slightly over 400. The curves of these figures show that when the hardened steels are tempered at 400 and 450 degrees Cent. (750 and 840 degrees Fahr.) their

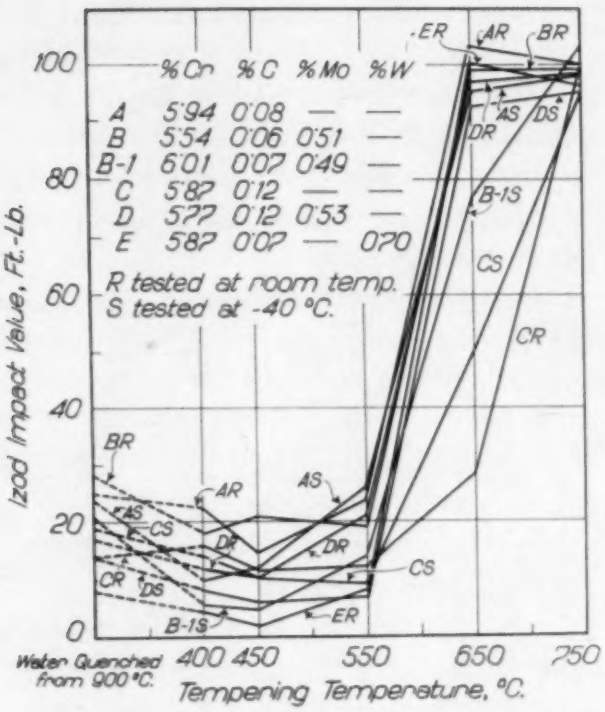


Fig. 2—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Tungsten.

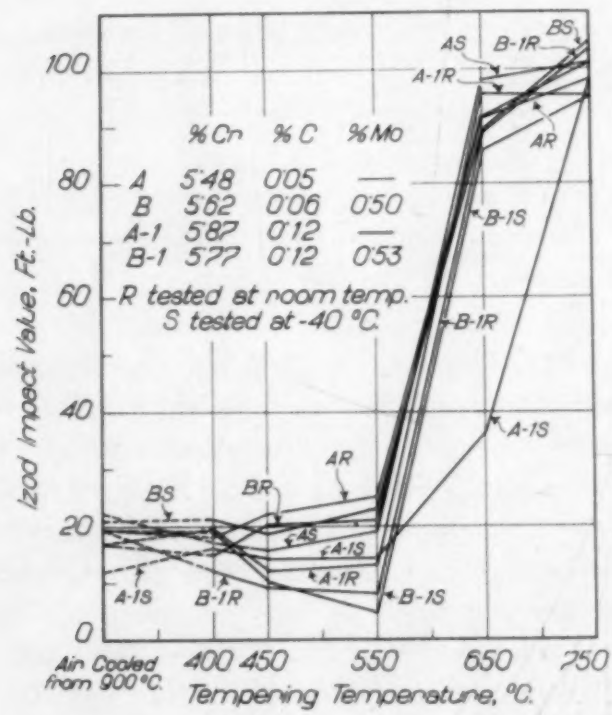


Fig. 3—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum.

toughness at room temperature is further adversely affected. In a few instances tempering at 550 degrees Cent. (1020 degrees Fahr.) caused a slight lowering of toughness but tempering at 650 and 750 degrees Cent. (1200 and 1380 degrees Fahr.) markedly improved the toughness. The tests made at —40 degrees Cent. revealed that most of the steels suffered an additional decrease in toughness after quenching or air cooling and tempering at 400, 450 and 550 degrees Cent. (750, 840 and 1020 degrees Fahr.) but as before, when the tempering temperatures reached 650 and 750 degrees Cent. (1380 degrees Fahr.) the metal exhibited a high degree of toughness. These results therefore indicate that all these wrought low carbon steels tend to lose impact resistance on heating for the 2-hour period at either 400 or 450 degrees Cent. (750 or 840 degrees Fahr.).

There is no further reference to the chromium steels containing tungsten in the remainder of this paper. These tungsten-containing steels are used to some extent in the wrought state, but more particularly in the cast condition. Such castings when given special heat treatments by the fabricators have high impact value, and retain this in service to such a degree that no troubles from this cause are encountered.

Silicon additions are frequently made to the 4 to 6 per cent chromium steels with and without molybdenum to enhance resistance to oxidation at elevated temperatures, and steels of this type were tested for toughness after treatment at the different temperatures. It was found, as shown in Figs. 4 and 5, that the presence of about 1.50 per cent silicon greatly reduced the toughness of the steels. The data show that the molybdenum-free 4 to 6 per cent chromium steel containing 1.49 per cent silicon has relatively low toughness at —40 degrees Cent. even after furnace cooling from 650 and 750 degrees Cent. (1200 and 1380 degrees Fahr.) following the quench or air cool from 900 degrees Cent. (1650 degrees Fahr.). The steel also exhibited low toughness at room temperature after the temper at 650 degrees Cent. (1200 degrees Fahr.), showing definitely that silicon produced an adverse effect. However, it is apparent that molybdenum has a strong tendency to counteract the adverse effect of silicon.

A thorough investigation was made of the nonhardenable 4 to 6 per cent chromium steels with and without titanium or columbium because of the possibility of securing steels that would retain their toughness after exposure to temperatures between 900 and

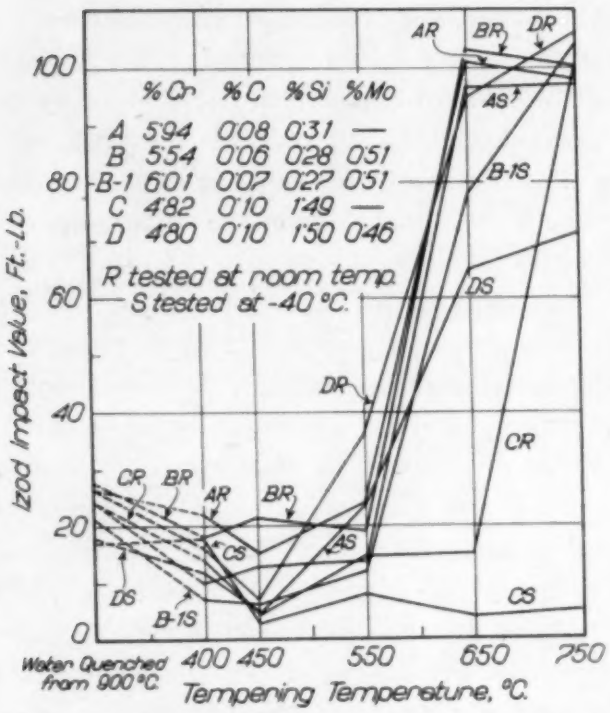


Fig. 4—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels of Low and High Silicon Content with and without Molybdenum.

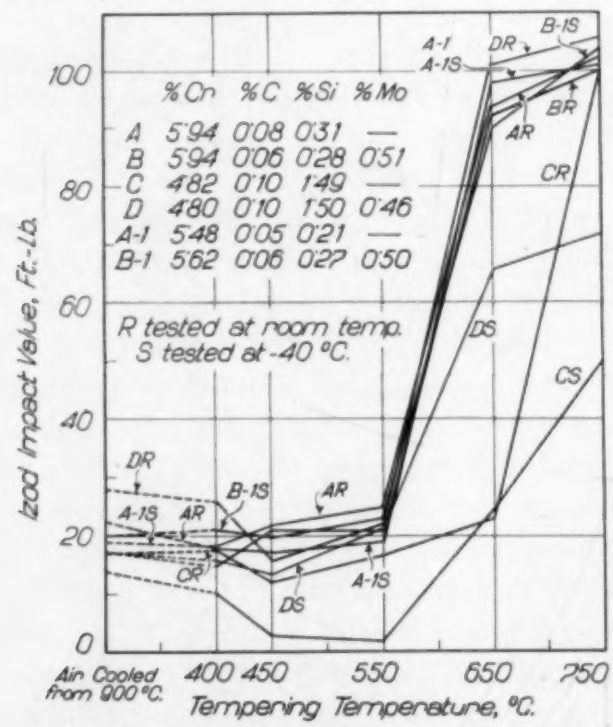


Fig. 5—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels of Low and High Silicon Content with and without Molybdenum.

—40 degrees Cent. This seemed probable because steels containing proper amounts of titanium or columbium can be heated at the higher temperatures for short periods without losing toughness and increasing in hardness, as is the case with the 4 to 6 per cent chromium steels with and without molybdenum. The titanium content was held between 4 and 7 times the carbon content, while the columbium content ranged between 6 and 10 times the carbon content and in every instance the carbon content of the steels was held at a maximum of 0.10 per cent.

To begin with, titanium-bearing 4 to 6 per cent chromium steels with and without molybdenum were respectively water-quenched and air-cooled from 900 degrees Cent. (1650 degrees Fahr.). As before, the steels were tempered at the different temperatures between 400 and 750 degrees Cent. (750 and 1380 degrees Fahr.) for 2 hours and furnace-cooled, and the results obtained are plotted in Figs. 6 and 7. Similar data previously obtained on the 4 to 6 per cent chromium steels are given for the sake of comparison.

In the quenched and air-cooled conditions the steels containing titanium gave Izod values from 90 to slightly over 100 foot-pounds but on tempering at 450 and 550 degrees Cent. (840 and 1020 degrees Fahr.) these values dropped to below 20 foot-pounds. Molybdenum additions markedly improved the steels, as observed in the tests conducted at room temperature. However, these steels exhibited little toughness at —40 degrees Cent. after tempering at 400, 450 and 550 degrees Cent. (750, 840 and 1020 degrees Fahr.), showing that although the steels containing titanium were relatively free of hardening they possessed low toughness after treatment in the range 400 to 550 degrees Cent. (750 to 1020 degrees Fahr.).

It was thought that the titanium-containing steels would retain their toughness to a greater extent in the annealed condition. Samples of the steels in this state were heated for 700 hours between 400 and 650 degrees Cent. (750 and 1200 degrees Fahr.) to duplicate approximately service conditions, and tested at room temperature and —40 degrees Cent. It was again noted as revealed by Fig. 8 that the steels lost toughness on account of the exposure to 400 450 and 550 degrees Cent. (750, 840 and 1020 degrees Fahr.). On the other hand, the steels containing both titanium and molybdenum were found to be quite tough under these conditions, and it is apparent that molybdenum greatly benefits the steels. The 4 to 6 per cent chromium steels without titanium lost some toughness after treat-

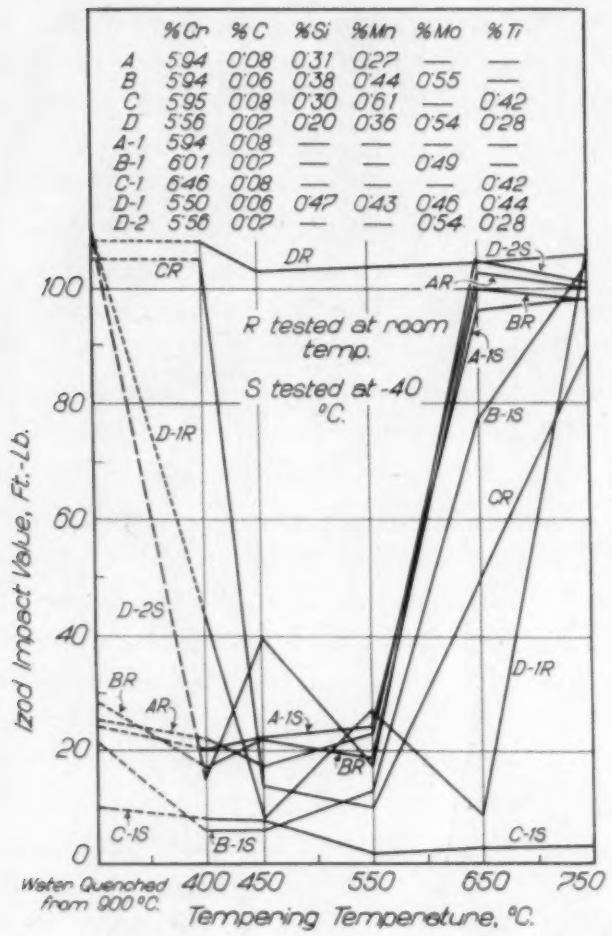


Fig. 6—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Titanium.

ment at 450 degrees Cent. (840 degrees Fahr.) but these did not depreciate in toughness to the same extent as those containing only titanium.

The hardness values obtained on the titanium-bearing steels that exhibited such low toughness are worthy of consideration and data of this type are given in Table I.

The low carbon 4 to 6 per cent chromium steels are relatively hard after air cooling from 900 degrees Cent. (1650 degrees Fahr.) and have a tendency to harden further on tempering for 2 hours at 450 degrees Cent. (840 degrees Fahr.). In the annealed condition the same steels exhibit no tendency to harden as a result of heating at any of the temperatures between 400 and 650 degrees Cent. (750 and 1200 degrees Fahr.). In contrast, the steels containing titanium are soft after air cooling from 900 degrees Cent. (1650 degrees

Table I

Hardness Tests on 4 to 6 Per Cent Chromium Steels Containing Titanium

	Per Cent			
Chromium	5.48	5.95	6.06	4.78
Carbon	0.05	0.07	0.08	0.06
Molybdenum	....	0.55	....	0.48
Titanium	....	....	0.42	0.30
Heat Treatment	Brinell Number	Brinell Number	Brinell Number	Brinell Number
Air-cooled from 900 degrees Cent.	302	351	128	137
Air-cooled from 900 degrees Cent. Tempered 2 hr. at 400 degrees Cent. and furnace-cooled	302	375	126	131
Air-cooled from 900 degrees Cent. Tempered 2 hr. at 450 degrees Cent. and air-cooled	321	387	126	124
Air-cooled from 900 degrees Cent. Tempered 2 hr. at 550 degrees Cent. and furnace cooled	286	255	124	121
Air-cooled from 900 degrees Cent. Tempered 2 hr. at 650 degrees Cent. and furnace-cooled	134	137	121	124
Air-cooled from 900 degrees Cent. Tempered 2 hr. at 750 degrees Cent. and furnace-cooled	128	143	121	137
Heated at 750 degrees Cent. 4 hr. and air-cooled	131	143	128	137
Heated at 750 degrees Cent. 4 hr. and air-cooled. Tempered 700 hr. at 400 degrees Cent. and furnace-cooled	124	149	126	143
Heated at 750 degrees Cent. 4 hr. and air-cooled. Tempered 700 hr. at 450 degrees Cent. and furnace-cooled	121	149	126	143
Heated at 750 degrees Cent. 4 hr. and air-cooled. Tempered 700 hr. at 550 degrees Cent. and furnace-cooled	121	146	126	137
Heated at 750 degrees Cent. 4 hr. and air-cooled. Tempered 700 hr. at 650 degrees Cent. and furnace-cooled	116	143	121	137

Fahr.) and their hardness does not noticeably change on heating at the different temperatures, which reveals that the loss in toughness exhibited by the steels after tempering at 400, 450 and 550 degrees Cent. (750, 840 and 1020 degrees Fahr.) is not accompanied by a definite change in hardness.

Decidedly different results were secured when similar treatments were applied to the columbium-bearing 4 to 6 per cent chromium steels. It was found, as shown in Figs. 9 and 10, that after quenching and air cooling from 900 degrees Cent. (1650 degrees Fahr.) these steels retained their toughness to a high degree both at normal and sub-zero temperatures after heating between 400 and 750 degrees Cent. (750 and 1380 degrees Fahr.) followed by furnace cooling. A slight drop in toughness was noted at —40 degrees Cent. after quenching from 900 degrees Cent. (1650 degrees Fahr). and tempering at 400 and 450 degrees Cent. (750 and 840 degrees Fahr.) but this was not of a serious nature. A good confirmation of this was obtained in the samples held for 700 hours at the different temperatures after air cooling from 900 degrees Cent. (1650 degrees Fahr.), which shows that the steels retain their toughness dur-

ing a long exposure to these temperatures. These latter data are presented in Fig. 11, and those of Fig. 12 show that in the annealed state there is little likelihood the steels will develop brittleness because of exposure to similar temperatures. These data are of considerable importance from a practical standpoint, since they indicate that the nonhardening columbium-containing 4 to 6 per cent chro-

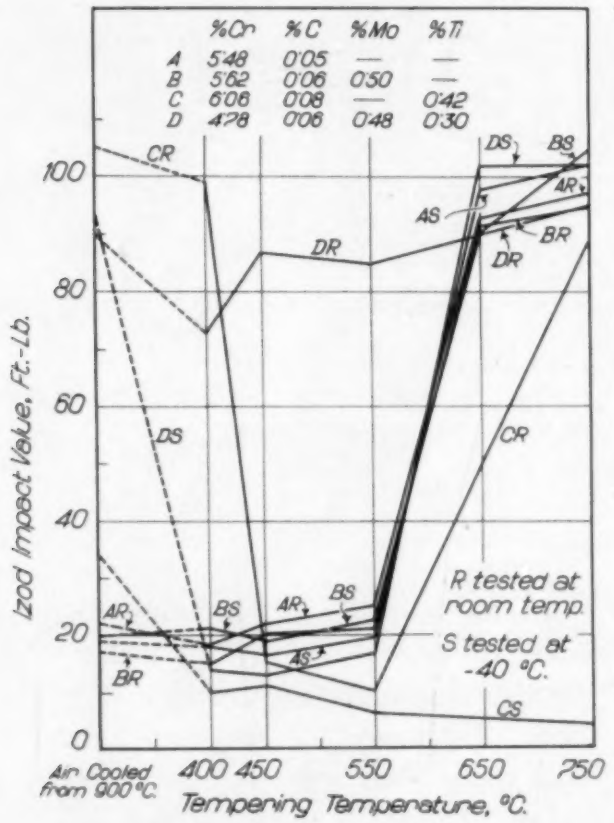


Fig. 7—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Titanium.

mium steels are relatively tough after exposure to temperatures between 750 and —40 degrees Cent. This should permit them to be used with greater safety than the plain 4 to 6 per cent chromium steels in applications in which the latter are now employed.

Brinell hardness values were obtained on the steels that were held for 700 hours at the different temperatures. These are given in Table II.

The data in this table are of particular interest because they show that on long holding at 400 degrees Cent. (750 degrees Fahr.) after air cooling from 900 degrees Cent. (1650 degrees Fahr.) the

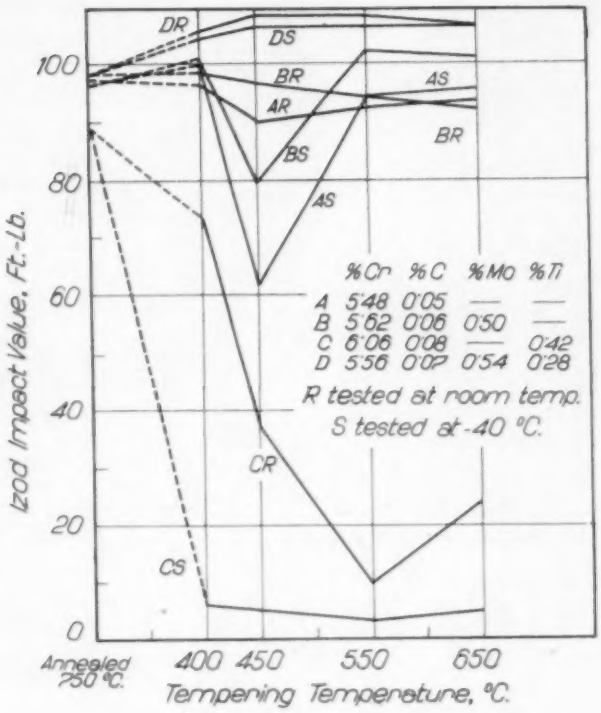


Fig. 8—Effect of Tempering for 700 Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Titanium.

Table II

Hardness Tests on 4 to 6 Per Cent Chromium Steels Containing Columbium

	Per Cent			
Chromium	5.87	5.95	5.52	5.49
Carbon	0.05	0.08	0.08	0.06
Molybdenum	....	0.55	....	0.50
Columbium	....	....	0.53	0.54

Heat Treatment	Brinell Number	Brinell Number	Brinell Number	Brinell Number
Air-cooled from 900 degrees Cent.	332	340	137	131
Air-cooled from 900 degrees Cent. Held 700 hr. at 400 degrees Cent. and furnace-cooled	340	364	131	137
Air-cooled from 900 degrees Cent. Held 700 hr. at 450 degrees Cent. and furnace-cooled	228	255	128	128
Air-cooled from 900 degrees Cent. Held 700 hr. at 550 degrees Cent. and furnace-cooled	166	174	118	126
Air-cooled from 900 degrees Cent. Held 700 hr. at 650 degrees Cent. and furnace-cooled	124	126	118	118
Air-cooled from 900 degrees Cent. Held 700 hr. at 750 degrees Cent. and furnace-cooled	126	128	118	118
Heated at 750 degrees Cent. 4 hr. and air-cooled	126	131	118	118
Heated at 750 degrees Cent. 4 hr. and air-cooled. Held 700 hr. at 400 degrees Cent. and furnace-cooled	137	137	121	128
Heated at 750 degrees Cent. 4 hr. and air-cooled. Held 700 hr. at 450 degrees Cent. and furnace-cooled	131	137	124	128
Heated at 750 degrees Cent. 4 hr. and air-cooled. Held 700 hr. at 550 degrees Cent. and furnace-cooled	126	143	128	126
Heated at 750 degrees Cent. 4 hr. and air-cooled. Held 700 hr. at 650 degrees Cent. and furnace-cooled	128	126	118	126

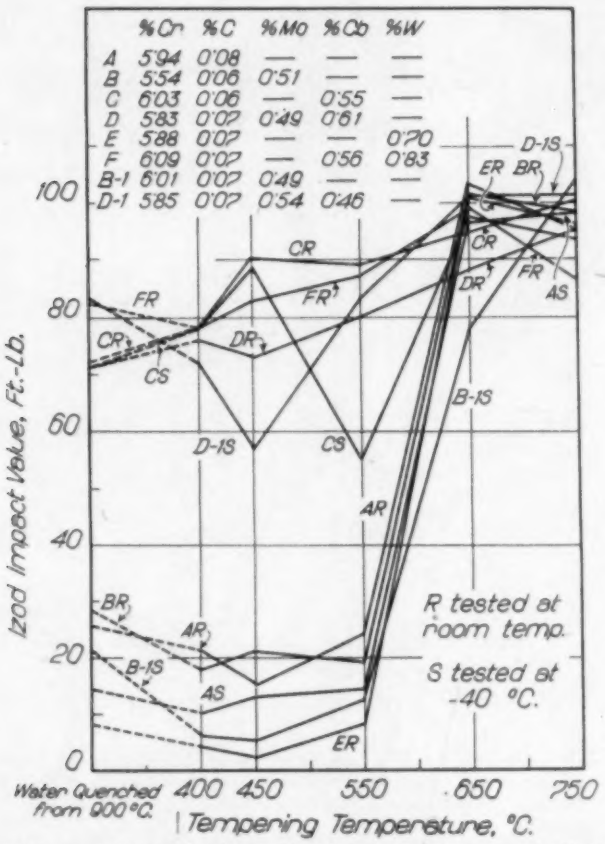


Fig. 9—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Columbium.

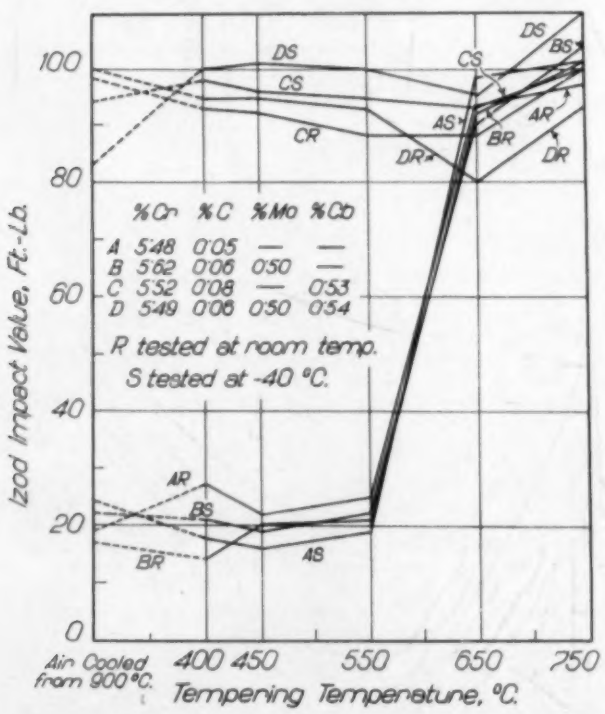


Fig. 10—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Columbium.

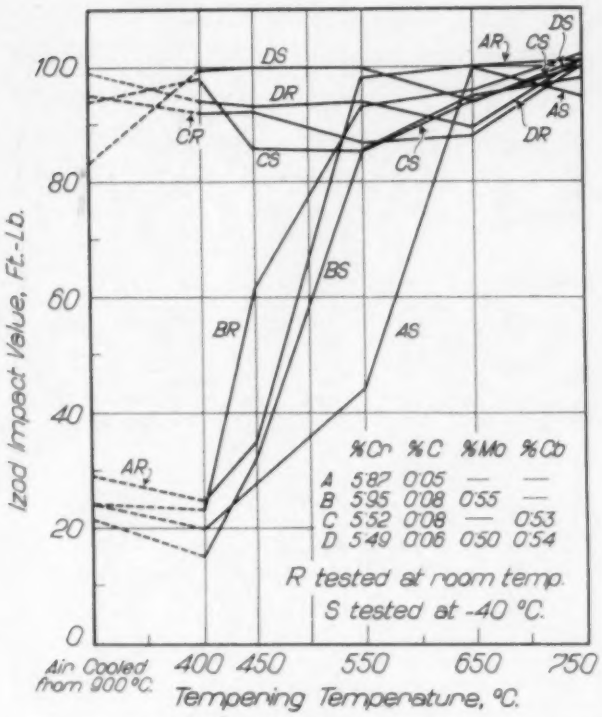


Fig. 11—Effect of Tempering for 700 Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Columbium.

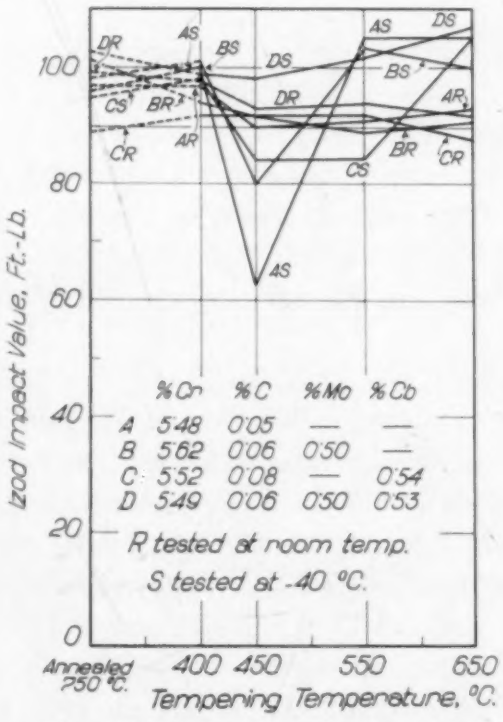


Fig. 12—Effect of Tempering for 700 Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Columbium.

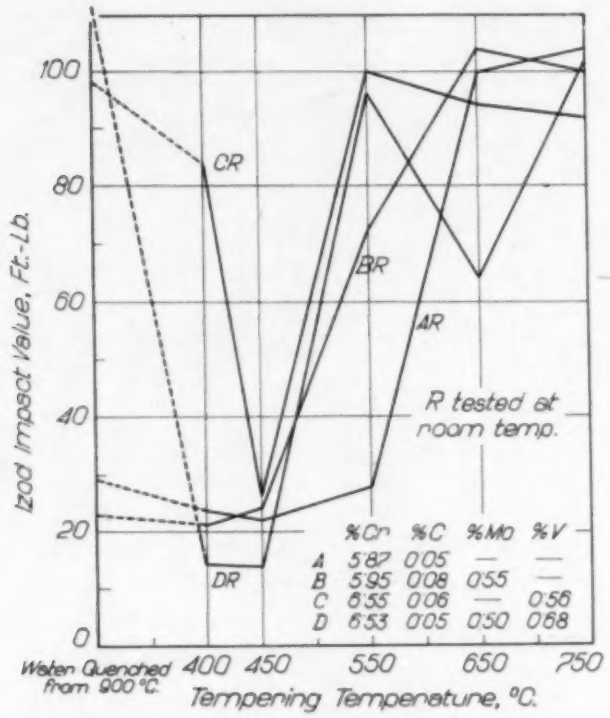


Fig. 13—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 4 to 6 Per Cent Chromium Steels with and without Molybdenum and Vanadium.

4 to 6 per cent chromium steels harden further to a noticeable degree. When the holding temperature is increased to 450 and 550 degrees Cent. (840 and 1020 degrees Fahr.) the steels become softer, as is the case when they are held at 650 and 750 degrees Cent. (1200 and 1380 degrees Fahr.). As was to be expected the columbium-containing steels were quite soft after treatment at all the temperatures between 900 and 400 degrees Cent. (1650 and 750 degrees Fahr.).

Tests were conducted on 4 to 6 per cent chromium steels to which vanadium was added to secure nonhardening properties. As before, the steels were heated at different temperatures and tested for toughness, and as shown in Fig. 13, they exhibited even greater loss in toughness than those containing titanium. This was associated with an increase in hardness that was especially noticeable after the temper at 450 degrees Cent. (840 degrees Fahr.). It was concluded that while vanadium would reduce the air hardening of the 4 to 6 per cent chromium steels, the metal was susceptible to the development of low toughness during exposure to 400 and 450 degrees Cent. (750 and 840 degrees Fahr.).

The final steels of the investigation contained between 2 and 3 per cent and 3 and 4 per cent chromium, and were of low carbon content. These steels were treated with the proper percentages of titanium and columbium, and tested for toughness after air cooling and quenching from 900 degrees Cent. (1650 degrees Fahr.). It was interesting to find that the low carbon 3 to 4 per cent chro-

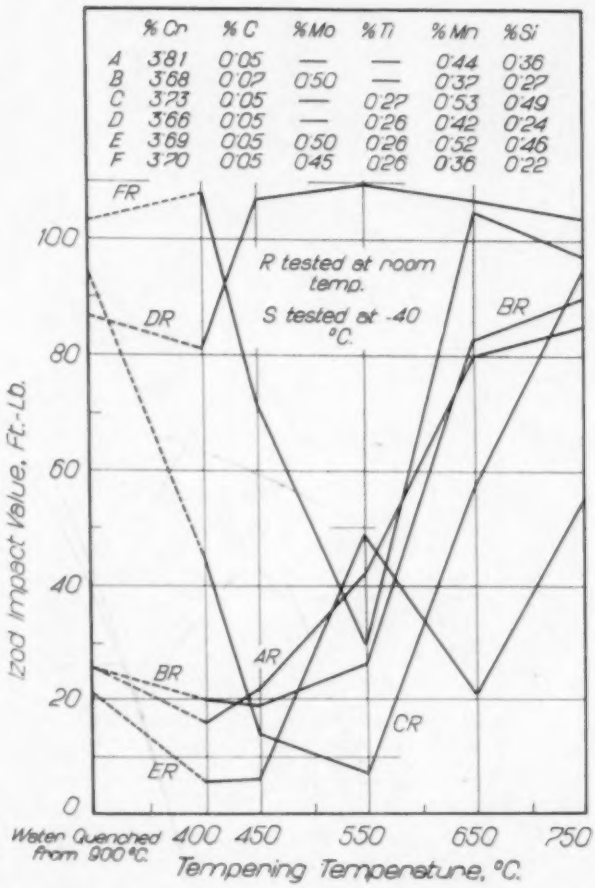


Fig. 14—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 3 to 4 Per Cent Chromium Steels with and without Molybdenum and Titanium.

mium steels were quite susceptible to hardening, especially if they were quenched from 900 degrees Cent. (1650 degrees Fahr.). The steels air-cooled from the same temperature were somewhat softer but even in this instance were fairly hard. The low carbon 2 to 3 per cent chromium steels were also hard after quenching from this temperature although they were left in a relatively soft state after air cooling. The data of Fig. 14 reveal that, as in the instance of the 4 to 6 per cent chromium steels, titanium fails to impart toughness, as determined by impact tests, to the 3 to 4 per cent chromium

steels even though they are relatively free of air hardening. The decrease in toughness that occurred in the steels on holding at 400, 450 and 550 degrees Cent. (750, 840 and 1020 degrees Fahr.) and furnace cooling took place without a marked change in hardness. Columbium additions yielded steels that were tough after treatment at all temperatures between 900 and —40 degrees Cent.

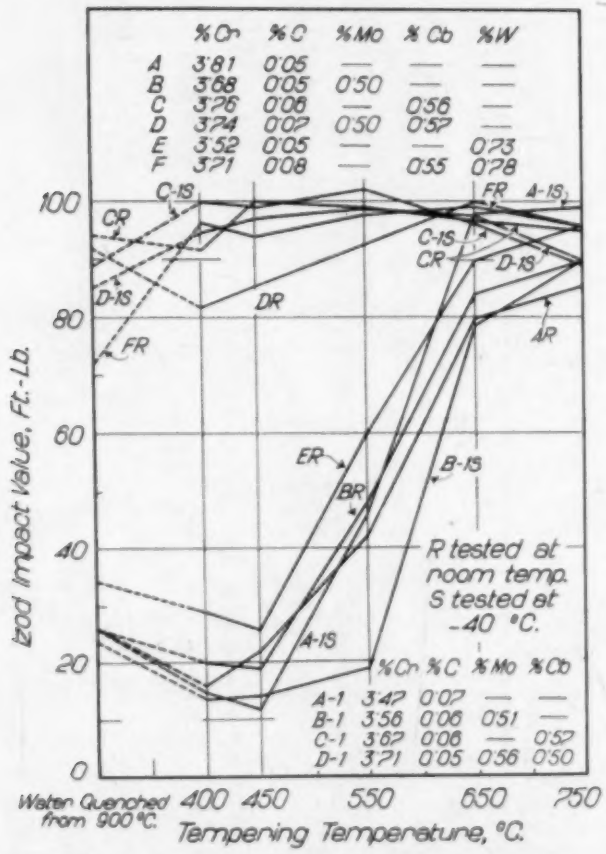


Fig. 15—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 3 to 4 Per Cent Chromium Steels with and without Molybdenum and Columbium.

Data on these latter steels are illustrated by Figs. 15 and 16, which also show that the 3 to 4 per cent chromium steels without columbium tend to decrease in toughness on tempering at 400 and 450 degrees Cent., particularly if they are exposed to —40 degrees Cent.

A study of Figs. 17 and 18 shows that the titanium addition actually reduces the toughness of the 2 to 3 per cent chromium steels when they are exposed to —40 degrees Cent. and, as in previous instances, molybdenum improves the toughness of the titanium-containing steels. A good indication of the effect of carbon is provided by the results obtained on the 0.03 per cent carbon steel con-

taining 2.60 per cent chromium. This steel exhibited considerable toughness after quenching from 900 degrees Cent. (1650 degrees Fahr.) and no decrease in this property occurred on tempering at 400 and 450 degrees Cent. (750 and 840 degrees Fahr.) and furnace cooling. The slightly higher carbon content steels were quite tough after air cooling from 900 degrees Cent. (1650 degrees Fahr.) but

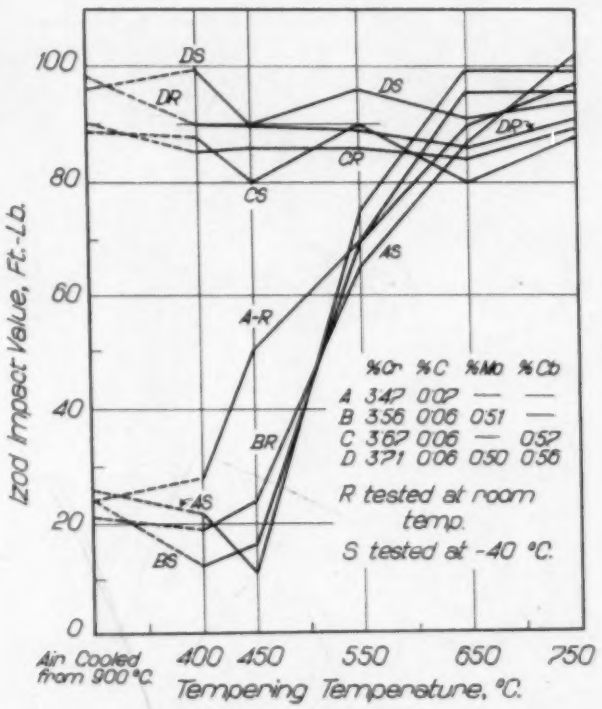


Fig. 16—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 3 to 4 Per Cent Chromium Steels with and without Molybdenum and Columbium.

these steels showed a slight decrease in toughness when exposed to 400 and 450 degrees Cent. (750 and 840 degrees Fahr.).

A high degree of toughness was obtained in the low carbon 2 to 3 per cent chromium steels by the addition of between 0.30 and 0.40 per cent columbium. It will be noted in Figs. 19 and 20 that while these steels are fairly tough after rapid cooling from 900 degrees Cent. (1650 degrees Fahr.) columbium enhances this property, and under conditions where toughness is important this element may be advantageously used.

After completing the experiments which showed that some of the steels retained their toughness at —40 degrees Cent., it was decided to continue the investigation employing still lower temperatures. Samples of the various steels with and without molybdenum

and columbium were fully annealed and subjected respectively to temperatures of —70, —100, and —120 degrees Cent. It was observed, as shown in Table III, that the plain chromium steels in the properly annealed condition retained a good deal of their toughness at temperatures down to —120 degrees Cent. The molybdenum and columbium-containing steels were also tough under these conditions

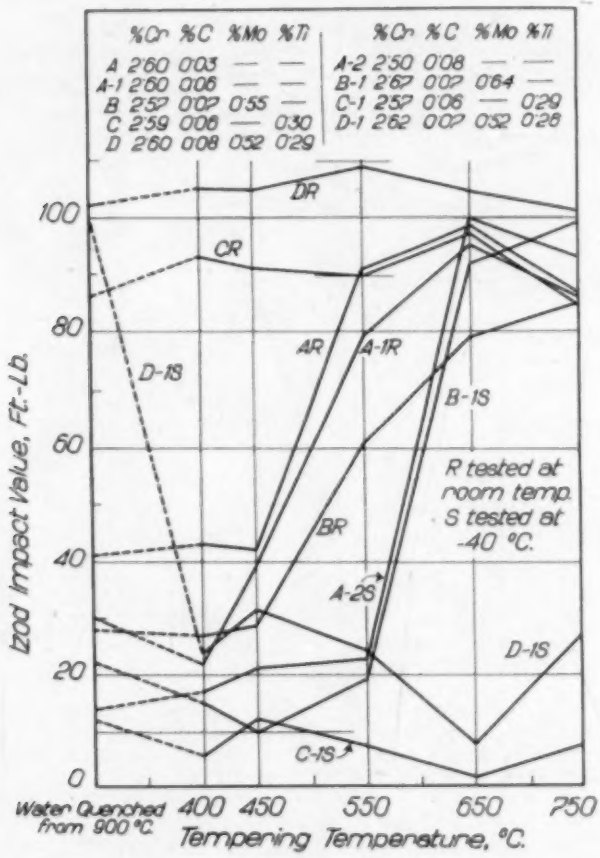


Fig. 17—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 2 to 3 Per Cent Chromium Steels with and without Molybdenum and Titanium.

but it was clear that these two additions added little to the low temperature toughness of the steels. At —183 degrees Cent. all the steels suffered a marked decrease in toughness.

It is evident from previous discussion that the addition of columbium to low carbon steels containing between 2 and 6 per cent chromium produces nonhardenable steels that retain their toughness when heated through a rather wide range of temperatures. In view of this, a brief description of other properties of these steels should be of interest. Table IV describes the tensile characteristics of the

Table III

Results of Low Temperature Tests on 3 to 6 Per Cent Chromium Steels

	Per Cent						
Chromium	3.07	3.47	3.56	5.96	5.97	5.72	5.60
Carbon	0.07	0.06	0.06	0.08	0.09	0.06	0.06
Molybdenum	....	0.50	....	....	0.50	....	0.54
Columbium	....	....	0.50	....	....	0.56	0.53
	Izod Impact, Ft.-Lb.						
Air-cooled from 900 degrees Cent. Held 3 hr. at 750 degrees Cent. and air-cooled. Tested at room temperature	77	90	80	89	96	81	86
Air-cooled from 900 degrees Cent. Held 3 hr. at 750 degrees Cent. and air-cooled. Tested at —40 degrees Cent.	78	90	92	96	102	99	99
Air-cooled from 900 degrees Cent. Held 3 hr. at 750 degrees Cent. and air-cooled. Tested at —70 degrees Cent.	90	98	96	99	104	98	103
Air-cooled from 900 degrees Cent. Held 3 hr. at 750 degrees Cent. and air-cooled. Tested at —100 degrees Cent.	92	102	100	104	104	101	105
Air-cooled from 900 degrees Cent. Held 3 hr. at 750 degrees Cent. and air-cooled. Tested at —120 degrees Cent.	100	57	105	86	107	105	108
Air-cooled from 900 degrees Cent. Held 3 hr. at 750 degrees Cent. and air-cooled. Tested at —183 degrees Cent.	2	3	1	2	2	2	1

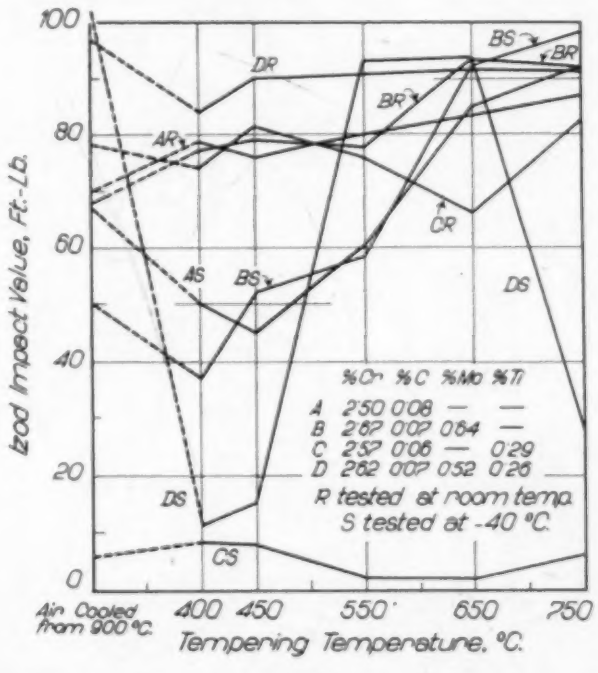


Fig. 18—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 2 to 3 Per Cent Chromium Steels with and without Molybdenum and Titanium.

steels in the annealed condition and after air cooling from 900 degrees Cent. (1650 degrees Fahr.). These data show that while the steels containing from slightly less than 4 to 6 per cent chromium are soft and ductile in the annealed condition, they are relatively hard

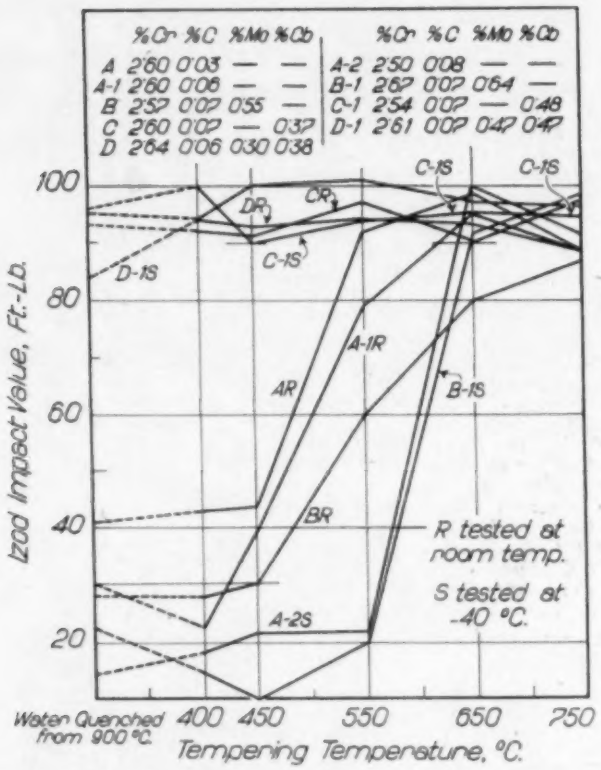


Fig. 19—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 2 to 3 Per Cent Chromium Steels with and without Molybdenum and Columbium.

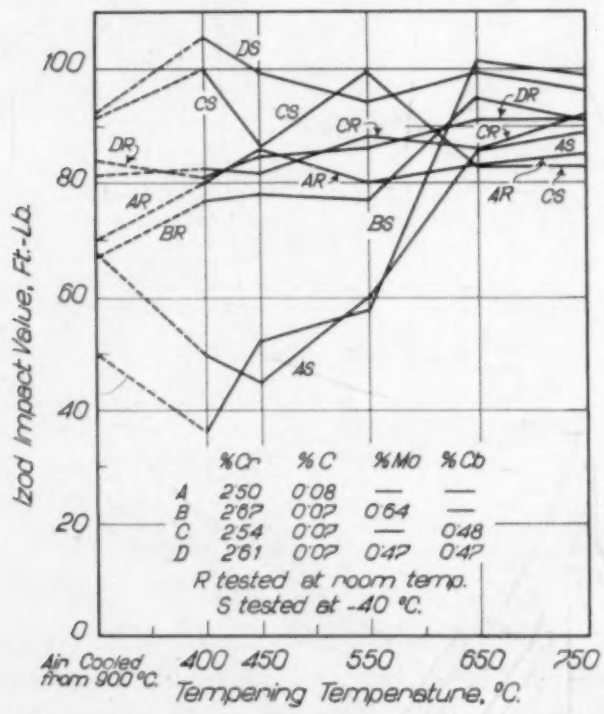


Fig. 20—Effect of Tempering for Two Hours at Different Temperatures on the Toughness of 2 to 3 Per Cent Chromium Steels with and without Molybdenum and Columbium.

and low in ductility after air cooling from 900 degrees Cent. (1650 degrees Fahr.). The steels containing columbium possess high ductility and are soft when treated similarly. The practical meaning of this is that if it is necessary to bend or otherwise shape plates, sheets, strip or bars these operations can be carried out by heating and subsequently cooling the columbium-bearing steels in air from about 900 degrees Cent. (1650 degrees Fahr.) without simultaneously causing them to become hard and low in toughness and ductility, as is the case with the plain chromium steels. The data in this table are of additional interest. The low carbon 2.50 per cent chromium steels exhibit little tendency to harden when air-cooled from 900 degrees Cent. (1650 degrees Fahr.), showing that about 3 per cent chromium is required to impart air hardening properties to the low carbon steels.

Table IV
Physical Tests on Wrought Chromium Steels Containing Columbium
(Standard Test Pieces Taken from ¾-In. Round Bars)

Per Cent										
Cr	C	Mo	Cb	Treatment	Yield Pt. p.s.i.	Max. Stress p.s.i.	Per Cent El. in 2 In.	Per Cent Red. in Area	Izod Impact Ft-Lb.	Brinell Number
2.65	0.06	....	....	No. 1	43,500	60,000	42	79	85	121
2.65	0.06	....	....	No. 2	46,500	68,000	35	72	69	166
2.57	0.07	0.55	....	No. 1	51,000	68,750	35	78	85	131
2.57	0.07	0.55	....	No. 2	62,350	101,000	24	51	54	192
2.53	0.09	....	0.56	No. 1	49,500	66,750	35	78	98	131
2.53	0.09	....	0.56	No. 2	46,000	66,100	40	79	88	124
2.61	0.07	0.49	0.55	No. 1	49,000	70,500	28	78	90	131
2.61	0.07	0.49	0.55	No. 2	46,400	61,850	37	81	91	124
3.67	0.06	....	....	No. 1	43,500	65,000	37	78	100	131
3.67	0.06	....	....	No. 2	56,500	91,000	25	50	58	286
3.68	0.07	0.50	....	No. 1	52,000	77,000	31	76	90	143
3.68	0.07	0.50	....	No. 2	82,000	112,000	12	28	27	290
3.76	0.06	....	0.56	No. 1	44,000	73,500	31	79	95	131
3.76	0.06	....	0.56	No. 2	45,000	67,000	43	85	84	120
3.74	0.06	0.51	0.47	No. 1	43,000	72,500	33	78	96	137
3.74	0.06	0.51	0.47	No. 2	39,000	65,000	42	84	82	118
6.03	0.08	....	....	No. 1*	54,000	83,500	31	74	91	153
6.03	0.08	....	....	No. 2	163,000	197,000	6	20	19	351
5.81	0.08	0.45	....	No. 1*	56,000	86,000	29	72	101	149
5.81	0.08	0.45	....	No. 2	143,000	173,000	4	16	12	340
6.06	0.08	....	0.58	No. 1*	39,000	72,000	36	78	90	146
6.06	0.08	....	0.58	No. 2	40,000	75,500	31	69	88	149
6.04	0.08	0.51	0.56	No. 1*	39,000	75,000	35	78	95	143
6.04	0.08	0.51	0.56	No. 2	41,000	76,000	31	70	89	149

Note: No. 1 Treatment = Heated at 750 degrees Cent. 2 hr. and air-cooled.
No. 2 Treatment = Air-cooled from 900 degrees Cent.
No. 1* Treatment = Heated at 750 degrees Cent. 4 hr. and air-cooled.

Frequently welding is required in fabricating equipment. The columbium-bearing 4 to 6 per cent chromium steels can be successfully welded with a chromium-nickel steel welding rod without en-

countering difficulty due to excessive hardening in the zones immediately adjacent to the weld. It is revealed by the photographs of Fig. 21 that the low carbon 4 to 6 per cent chromium steel containing molybdenum hardens appreciably in the zones adjacent to the weld, which is due to the air hardening characteristics of the steel. Experi-

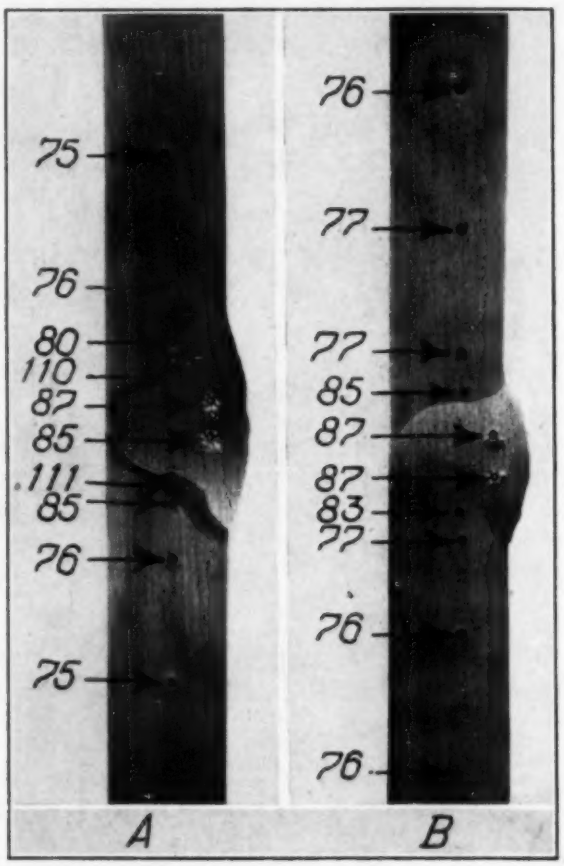


Fig. 21—Rockwell "B" Hardness Values on Welded 4 to 6 Per Cent Chromium Steels with and without Columbium. Welded with a 24 Per Cent Chromium—12 Per Cent Nickel Steel Rod. "A" Arc Weld Made in Annealed One-Half Inch Plate of Steel Containing 5.09 Per Cent Chromium, 0.46 Per Cent Molybdenum and 0.07 Per Cent Carbon. "B" Arc Weld Made in Annealed One-Half Inch Plate of Steel Containing 5.82 Per Cent Chromium, 0.53 Per Cent Molybdenum, 0.51 Per Cent Columbium and 0.06 Per Cent Carbon. The Columbium-Bearing Steel is Relatively Free of Hardening in Zones Adjacent to Weld.

ence has shown that it is advisable to anneal welded structures of these steels to be sure that serious difficulties are not encountered because of the hardening. The welds produced in the columbium-bearing 4 to 6 per cent chromium steels with the 24 per cent chromium and 12 per cent nickel steel rods possess a high degree of ductility and toughness and the metal is not greatly hardened in the

adjacent zones. Izod impact values of at least 35 foot-pounds will be obtained in these welds and in the adjacent zones, showing that the unannealed welds are sufficiently tough for many purposes. If intergranular corrosion in the weld metal is involved the welding should be done with a columbium-bearing steel rod containing similar percentages of chromium and nickel.

Another improvement resulting from the columbium addition is an enhancement in oxidation resistance. As implied earlier, columbium combines with the carbon present in the steels and the carbides formed no longer function like chromium carbides or the double carbides of chromium and iron that may exist in the plain chromium steels. The result is to release chromium from carbide formation, which permits more of this element to enter the solid solution and exert its favorable influence. The data given in Table V were secured in tests made in a strictly oxidizing atmosphere on samples that consisted of solid cylinders 7/8 inch in diameter by 1¼ inch long. The samples were furnace cooled after exposure to the temperatures indicated, and the percentage loss of weight determined. The figures given clearly show that columbium improves the heat resistance of the steels.

Table V
Oxidation Tests on Chromium Steels Containing Columbium

Per Cent				Per Cent Loss in Weight After Exposure for 1000 Hr. at 640 to 650 Degrees Cent.	Per Cent Loss in Weight After Exposure for 900 Hr. at 720 to 730 Degrees Cent.
Cr	C	Mo	Cb		
....	0.15	....	....	8.16	26.50
2.60	0.07	....	....	3.40	16.80
2.57	0.07	0.55	....	3.79	19.32
2.54	0.06	....	0.57	2.42	12.25
2.61	0.07	0.49	0.56	3.20	16.00
3.49	0.07	....	....	2.98	10.90
3.47	0.06	0.50	....	2.74	10.40
3.55	0.06	....	0.55	1.71	6.20
3.83	0.08	0.53	0.51	1.22	5.60
5.96	0.08	....	....	0.39	6.10
5.97	0.09	0.55	....	0.20	5.40
6.03	0.08	....	0.69	0.10	0.87
5.87	0.09	0.52	0.52	0.10	0.70

The effect of columbium on the creep strength of the 4 to 6 per cent chromium steels at elevated temperatures is of importance, and data in this connection are given in Fig. 22. These data were obtained in creep tests made according to the weigh bar method, and they indicate that columbium has practically no effect on strength at

moderately high temperatures even though, as previously shown, columbium appears to reduce the strength of the steels at room temperatures slightly. Molybdenum, however, increases the creep strength of the columbium-bearing steels to a marked degree, especially at temperatures of 538 degrees Cent. (1000 degrees Fahr.). The value given at 648 degrees Cent. (1200 degrees Fahr.) for the

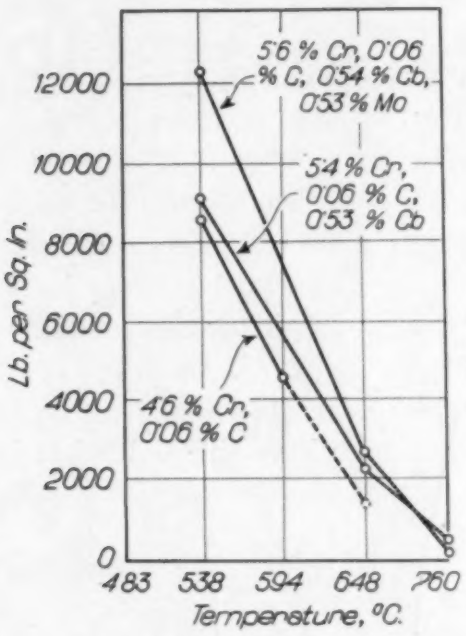


Fig. 22—Creep Strength at Various Temperatures of 4 to 6 Per Cent Chromium Steels with and without Columbium and Molybdenum. (1 Per Cent in 10,000 Hours).

plain 4 to 6 per cent chromium steel is purely an approximation because data on the creep strength of the steel by this method were not available. This explains why a part of the curve is drawn using dash lines.

Summary

This investigation has revealed that columbium additions to wrought steels containing between 2 and 6 per cent chromium and up to about 0.10 per cent carbon with normal manganese and silicon contents, enhance their toughness under conditions that involve exposure for either long or short periods at temperatures between 750 and —40 degrees Cent. The columbium-bearing steels can be cooled either fast or slowly from temperatures within this range without developing low toughness.

Columbium reduces the air hardening characteristics of the low carbon 3 to 6 per cent chromium steels, which permits them to be heated as may be required in fabrication to temperatures in the neighborhood of 900 degrees Cent. (1650 degrees Fahr.) or slightly higher for short periods and air-cooled without greatly increasing in hardness. The steels retain their toughness both at room temperature and at —40 degrees Cent. after such treatment, which indicates that if excessive heating should occur in service or if it is necessary to make repairs, difficulties are not likely to occur because of low toughness.

The steels containing columbium can be welded using an austenite chromium-nickel steel rod of the 24-12 or 25-20 type, and a high degree of ductility and toughness can be obtained in the weld and the adjacent zones. If the welds are exposed to corrosive conditions in the range 300 to 700 degrees Cent. (570 to 1290 degrees Fahr.) the welding rods should also contain columbium.

Columbium improves the oxidation resistance of the 3 to 6 per cent chromium steels at temperatures as high as 700 to 750 degrees Cent. (1290 to 1380 degrees Fahr.) and does not detrimentally affect the creep strength of the 4 to 6 per cent chromium steels at 538 and 594 degrees Cent. (1000 and 1100 degrees Fahr.) even though the strength of the steels at normal temperatures appears to be slightly lowered.

These improvements are obtained in 0.10 per cent maximum carbon steels containing 3 to 4 and 4 to 6 per cent chromium, and from 6 to 10 times as much columbium as carbon. Columbium additions equivalent to at least 5 times the carbon content are edequate for enhancing the properties of the 2 to 3 per cent chromium steels. Molybdenum has been found to be a valuable addition to the columbium-bearing 4 to 6 per cent chromium steels as it imparts enhanced resistance to creep at moderately high temepratures.

Other additions such as titanium or vanadium will reduce the air hardening in similar steels, but these steels do not retain their toughness like those containing columbium. In the properly hot-worked condition the columbium-bearing low chromium steels retain toughness which together with the other valuable attributes should render them highly useful to industry.

Acknowledgment

The author desires to express his appreciation for the co-opera-

tion received from the management and members of the staff of the Union Carbide and Carbon Research Laboratories, Inc. James Thompson and W. L. Harbrecht were of great assistance in the making and hot working of the steel ingots. Mr. Thompson also assisted in connection with the actual testing of the steels, as did F. E. Bacon. T. R. Cunningham and his associates should be mentioned for their help in analyzing the different steels.

DISCUSSION

A. F. BRAID:[1] I would like to ask the author what the loss in columbium is, if any, on columbium-welded steels.

RUSSELL FRANKS: Yes, there is some. The average loss of columbium during welding does not exceed 25 per cent. This means that 75 per cent of the columbium in the rod is retained in the weld.

G. F. COMSTOCK:[2] Is there any theoretical explanation of the effect of columbium in reducing the brittleness after holding the temperature as Mr. Franks showed, and, if so, why does columbium have that effect?

RUSSELL FRANKS: I can only express an opinion in regard to that question. Columbium seems to precipitate the carbon as carbide out of the solid solution of ferrite without at the same time increasing the grain size. There are several other alloying elements that will give freedom from brittleness, but in so doing you get a material with increased grain size, which is likely to develop brittleness at low temperature; in other words, the columbium-bearing steels containing 4 to 6 per cent chromium steel are relatively free of air hardening and have fine grains, whereas with some of the other elements this is not the case.

R. E. BANNON:[3] I could not quite make out from the slides how much columbium was in the steels containing columbium alone.

RUSSELL FRANKS: The steels contain about one-half of one per cent of columbium, which is six to eight times the carbon content.

V. N. KRIVOBOK:[4] I was very much interested in the paper, also in the explanation given to Mr. Comstock. I wonder if this possibility has been considered: It seems that the carbides of columbium are relatively easily precipitated. Is it not possible that they go back into solution with difficulty, hence depriving the matrix of the necessary carbon which would confer the hardening properties? I believe it has been demonstrated that carbides of various elements dissolve in austenite at different rates. Unfortunately I have not studied the columbium carbide.

RUSSELL FRANKS: I might add this to what Dr. Krivobok has said. The information given here this afternoon has been on the low carbon wrought steels; so far we have not been able to successfully use columbium in cast 4

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[2]Metallurgical engineer, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.
[3]Metal and Thermit Corp., Carteret, N. J.
[4]Allegheny-Ludlum Steel Corp., Brackenridge, Pa.

to 6 per cent chromium steels because of the fact that the castings obtained do not have sufficient toughness for some purposes. For other purposes they might be perfectly all right, but as a rule the cast columbium-bearing 4 to 6 per cent chromium steels are not as tough as we would like to have them. Our investigations have shown that once the columbium carbide is formed, it precipitates in the casting at the grain boundary and remains there. It also precipitates in other parts of the steel. We have done some work along the lines Dr. Krivobok is thinking about. We have endeavored to improve the toughness by heating the steel up as high as 1200 degrees Cent., but have not been successful in securing a solution of the columbium carbide. In low carbon 4 to 6 per cent chromium steels containing vanadium, it is apparent that the vanadium carbide is soluble enough because if the temperature increases enough, there is an improvement in the toughness of the steels containing vanadium. However, the high vanadium content steels possess other defects.

V. N. KRIVOBOK: Is the hardenability increased?

RUSSELL FRANKS: Yes. The hardenability is somewhat increased.

V. N. KRIVOBOK: In other words, there is a possibility that the explanation based on solubility is a correct one.

RUSSELL FRANKS: Yes, but we cannot take enough of the columbium carbide into solid solution at 1200 degrees Cent. to obtain the desired result.

V. N. KRIVOBOK: Then you cannot, in your opinion, drive carbides into solution even at 1200 degrees Cent?

RUSSELL FRANKS: I only refer to columbium carbides.

V. N. KRIVOBOK: That bears out our experience quite nicely.

R. E. BANNON: This question is directed both to Mr. Franks and also to Dr. Krivobok: Do you mean to say you found that titanium carbide goes into solution quite readily, or does it approach columbium in this respect?

RUSSELL FRANKS: Titanium carbide is not as insoluble as columbium carbide. At 1200 degrees Cent. I believe you can take in at least half of the titanium carbides present in the steel.

Another indication of this is shown by the fact that in austenitic steels of the 18-8 type you can take titanium carbide into solid solution much more easily than you can columbium carbide; we have established that very definitely.

V. N. KRIVOBOK: I would like to start a friendly argument; I should like to hear from someone in this audience, to tell me whether or not they have definite proofs regarding first the existence and also the nature of both titanium and columbium carbides? Has anybody done work which definitely proves that in titanium-bearing steel we find titanium carbide?

RUSSELL FRANKS: Yes, we have done quite a little work.

V. N. KRIVOBOK: How do you know they are carbides?

RUSSELL FRANKS: We have actually separated the carbides after dissolving the steel away and have made a carbon determination on the residue; and the carbon found in the residue agrees with that obtained on the sample analyzed for carbon by the usual procedure.

R. E. BANNON: So you feel definitely sure that you do have carbides?

RUSSELL FRANKS: Yes, we feel quite sure about that.

A NEW 70/30 NICKEL-COPPER ALLOY SUBJECT TO PRECIPITATION HARDENING

By Erich Fetz

Abstract

This paper briefly discusses the various types of 70/30 nickel-copper alloys rendered subject to precipitation hardening by the addition of one or more elements.

The writer's former research work on copper-nickel-tin is extended to the 70/30 nickel-copper composition. The precipitation hardening effects in this alloy in relation to rising tin additions up to 20 per cent, to aging temperature and to time up to 1000 hours were investigated. The capacity of tin-containing 70/30 nickel-copper for plastic deformation and the softening characteristics of pure cold-worked 70/30 nickel-copper were studied in conjunction with the problem of superimposition of strain hardening and precipitation hardening effects.

THE physical properties of the alloys of the copper-nickel-tin type have been recently the subject of a series of investigations (1-6).[1] However, this research was restricted to a maximum nickel content of 40 per cent. Precipitation hardening tests of this author disclosed the formerly established homogeneity range of the alpha-solid solution of the ternary copper-nickel-tin system to be incorrect at several points.

Regarding the binary systems bounding the ternary constitutional diagram, the copper-tin and nickel-copper diagrams have been the subject of a great number of investigations. Only two complete studies of the nickel-tin system were available (and these were 30 years old, and contradictory) until two recent investigations partly (7) and completely (8-11) based on X-rays were made. From a technological point of view, the revision of the alpha-phase boundary line represents the most important feature of the latest research on nickel-tin alloys.

It had been briefly announced previously (12) that the range of copper-nickel-tin alloys responding to precipitation hardening treat-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The author, Erich Fetz, is research metallurgist, Wilbur B. Driver Co., Newark, N. J. Manuscript received June 25, 1938.

ments is much larger than could be expected on the basis of former investigations, the most extensive of which was made by Wise (13). In Fig. 1 are given the contributions of the various investigators and the new provisional alpha phase boundary lines. A confirmation by

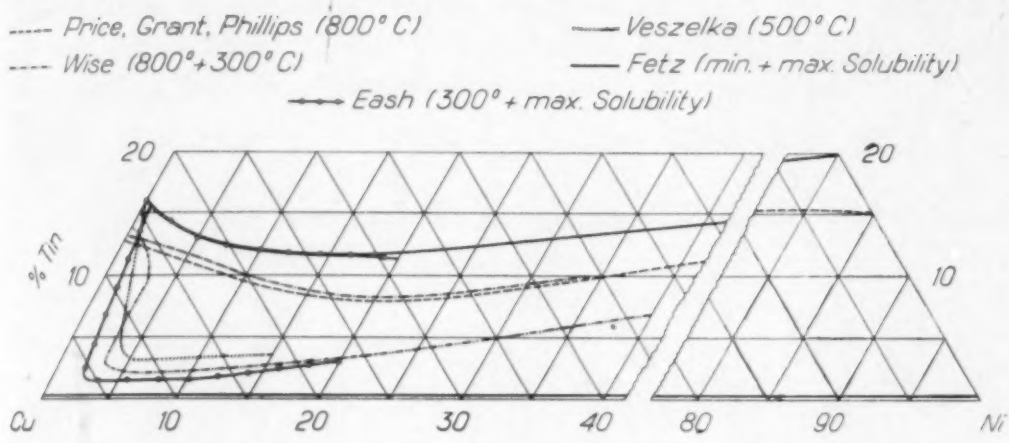


Fig. 1—Homogeneity Range of the Alpha Phase of the Copper-Nickel-Tin System.

X-rays is underway (14). The ternary constitutional diagram indicates that solid solutions of copper and nickel of any proportion should theoretically respond to precipitation hardening treatments after the addition of a reasonable amount of tin.

Among the cupro-nickels with over 40 per cent nickel, the 70/30 nickel-copper composition probably represents the most important one. It has gained considerable commercial importance under the trade name of "Monel" metal in honor of the inventor of the "natural" alloy which always contains some iron, manganese, silicon and carbon. In recent years, the original Monel composition has been modified and several precipitation hardening Monel metals have been discovered. In view of these important developments, an extension of the former experiments on copper-nickel-tin alloys beyond the 40 per cent nickel limit seemed to offer interesting theoretical and commercial possibilities.

Precipitation Hardening Monel Metals

As early as 1914, the hardening effect of aluminum upon the copper-nickel solid solution was noted by Read and Greaves (15, 16) who found in alloys containing maximum nickel and aluminum contents of 10 per cent "the separation of a second constituent from homogeneous copper-nickel solid solutions." Further studies of the

ternary copper-nickel-aluminum alloys were made by Austin and Murphy (17), Jones, Pfeil and Griffiths (18) and Brownsdon, Cook and Miller (19). However, the development of precipitation hardening aluminum-Monel was largely the work of Mudge and Merica, (20) while Fuller (21) obtained a patent on Monel metal to which aluminum plus carbon is added. Although a patent covering the age-hardening treatment of aluminum-Monel was filed as early as

Table I

Precipitation Hardening Effects in Beryllium-Monel

(After Masing and Pocher)

% Be	Brinell Hardness As Quenched	Fully Aged	Maximum Brinell Hardness Gain	Aging Treatment After Quenching from 950° C.
0.0	110	116	6	
0.5	126	134	8	500° C.—30 min.
1.0	141	331	90	500° C.—60 min.
1.5	164	425	261	500° C.—60 min.
2.0	190	460	270	500° C.—60 min.

1924, (22) the kinetics of the precipitation hardening process is not fully understood yet. Mudge and Merica assume that the "heat treatment effect is due to a transformation above 1100 and 1500 degrees Fahr. (595 and 815 degrees Cent.) probably—although not certainly—due to a variation in solid solubility of a second alloy constituent." The composition of the precipitating phase is unknown. It is "probably the solid solution of NiAl-Cu_3Al in various proportions" described by Austin and Murphy (17). Additions of 3-5 per cent aluminum are employed in the commercial alloys, which are naturally harder and more difficult to work than ordinary Monel metal. Maximum strength values of 160,000 pounds per square inch (330 Brinell) are reported for a fully hardened 4 per cent aluminum-Monel alloy.

Masing and Pocher (23) studied age-hardening 70/30 nickel-copper containing additions of beryllium. The maximum precipitation hardening effects in relation to rising beryllium concentrations in the 70/30 alloy quenched from 950 degrees Cent. (1740 degrees Fahr.) are given in Table I. The investigators state that Ni_2Bi_3 with some copper in solid solution is in equilibrium with the alpha phase in ternary alloys with over 2.5 per cent beryllium. Whereas copper and nickel dissolve 2.3 and 2.4 per cent beryllium respectively, the maximum solubility of nickel-copper solid solutions with 60 and 80

per cent nickel amounts to only 0.8 and 1.1 per cent beryllium respectively. The rolling properties of the two-phase alloys were found to be poor. A certain improvement of rollability and ductility was noticed when beryllium of higher purity was utilized, but the maximum precipitation hardening then dropped by about 50 Brinell. Recent experiments of Ballay (24) were restricted to Monel metal containing 1.1 per cent beryllium. Maximum age hardnesses of 393 and 420 Brinell were obtained in quenched and wrought alloys respectively.

Corson (25) obtained a patent on nickel-copper solid solutions with 40 to 70 per cent nickel rendered subject to precipitation hardening treatments by virtue of 1.5 to 10 per cent silicon additions. It appears doubtful that Monel metal with 3.5 per cent silicon can be softened to 95 Brinell by quenching from above 900 degrees Cent. (1650 degrees Fahr.). According to Corson, aging for 1 to 24 hours at 500 to 700 degrees Cent. (930 to 1290 degrees Fahr.) raises the hardness to 285 Brinell, and 145,000 pounds per square inch tensile strength at 10 per cent elongation were obtained. At 3 per cent silicon, silicides appear in the quenched alloy (26). This critical content is shifted to lower concentrations if the copper or iron content, or both, is increased. The precipitation hardening effects become appreciable only if the silicon content is raised to 3.5 to 4.25 per cent. Maximum hardnesses of 300 to 350 Brinell are reported. The effect of an increased copper content on the hardness of 3.25 per cent silicon-Monel is as follows:

	Brinell Hardness As			Hardness Gain Over Annealed State
	Cast	Quenched	Aged	
Copper content as in Monel metal	180	116	228	112
Monel + 3 per cent Copper	240	149	286	137

According to Kroll (27), Monel metal can be made precipitation hardenable by adding magnesium plus carbon and will yield a maximum strength of 143,000 pounds per square inch. No further information is given except that the precipitation hardening effects of nickel containing magnesium plus carbon (see Table II) are reduced by about 20 per cent by the addition of copper.

A patent on precipitation hardening Monel metal alloyed with titanium has been recently granted to Pilling and Merica (28). The solid solution hardness of a Monel metal type alloy with 63.4 per cent nickel, 27.2 per cent copper and 3.1 per cent iron was increased from

130 Brinell to 237 Brinell due to age hardening induced by 1.9 per cent titanium. Further data on the quantitative hardening effects of varying titanium additions as well as information on the precipitating phase and on the homogeneity range of the alpha phase are not available yet to the best of the author's knowledge.

Table II

Hardness of Magnesium and Carbon-Bearing Nickel Quenched from 1100 Degrees Cent. and Aged at 500 Degrees Cent.

(After Kroll)

	0.07%	0.1%	0.15%	0.2%	0.4% C.
0.0% Mg	100	108	108	110	125 Brinell
1.0% Mg	320	320	335	370	390 Brinell
Hardness Gain	220	212	227	260	265 Brinell

The alpha-phase boundary of the ternary system copper-nickel-indium has been recently established by Weibke and Pleger (29) and moderate precipitation hardening effects have been obtained in two 70/30 alloys in which either 10 per cent nickel or 10 per cent copper was replaced by 10 per cent indium.

70/30 Nickel-Copper Alloyed With Tin

Materials and Methods—The experimental alloys used in this investigation were melted in a high-frequency induction furnace in a clay-graphite crucible. Melts of 333 grams were made of oxygen-free, high conductivity copper, purified electrolytic nickel (99.866 per cent nickel) and high purity tin containing 0.003 per cent lead and 0.002 per cent iron. Owing to its high boiling point of 2363 degrees Cent. (4285 degrees Fahr.) and its peculiar vapor pressure curve, tin, in spite of its low melting point, could be melted together with the nickel and copper without appreciable losses. Shortly before casting into cast iron flat molds, the melts were deoxidized with 0.1 per cent magnesium. Rising amounts of tin of 5, 10, 15 and 20 per cent were added to a base alloy of 70 per cent nickel and 30 per cent copper. The tin additions depress the nickel and copper concentrations according to Table III. The chill cast alloys were tested for hardness with the standard Rockwell machine. The hardness numbers were converted into the more commonly used Brinell numbers using the formulas of Petrenko (30). The 5½x2½x¼-inch slabs were solution annealed at 1000 degrees Cent. (1830 degrees Fahr.)

for 30 minutes without using any special furnace atmosphere, water-quenched, ground on an emery belt and again tested for hardness. Precipitation hardening treatments were carried out in the temperature range of from 400 to 550 degrees Cent. (750 to 1020 degrees

Table III
Composition of Experimental Nickel-Copper-Tin Alloys

Melt No.	Nickel Per Cent	Copper Per Cent	Tin Per Cent
1	70	30	0
2	66.5	28.5	5
3	63	27	10
4	59.5	25.5	15
5	56	24	20

Fahr.) using temperature intervals of 50 degrees Cent. and annealing times of at least 300 hours. Some samples were subjected to cold rolling in order to study the cold workability of the new alloys. A few exploratory 1000-hour aging treatments were applied to samples in the cold-rolled condition.

Results

Solid Solution Hardness—The effect of rising additions of tin upon the solution hardness of the 70/30 nickel-copper base alloy, quenched from 1000 degrees Cent. (1830 degrees Fahr.) after a 30-minute anneal, is shown in Fig. 2, curve a, while curve b represents the as-cast hardnesses. The alloys high in tin were evidently softened considerably by the annealing treatment. For purposes of comparison, the hardening of pure nickel by rising additions of tin (8) is given in curve c, (as cast) and d, (annealed) while curve e shows the increase of hardness of copper by alloying it with tin. Although the initial hardness of the 70/30 nickel-copper solid solution is higher than of pure nickel, the alloy hardening by increasing amounts of tin is less pronounced in the 70/30 nickel-copper base alloy than in pure nickel so that both hardness curves intersect. Copper evidently improves the workability of plain nickel-tin alloys. It is noteworthy that the rate of hardening by rising tin concentrations is materially less in the binary copper-tin bronzes than in nickel-tin alloys. The hardness of copper, 70/30 nickel-copper and nickel is increased by every 1 per cent of tin respectively by 2.8, 4.4 and 8.1 Brinell units.

Precipitation Hardening Effects

Quenched Alloys—Figs. 3, 4 and 5 show respectively the course of hardness variations at 450, 500 and 550 degrees Cent. (840, 930 and 1020 degrees Fahr.) during a 300-hour heat treatment.

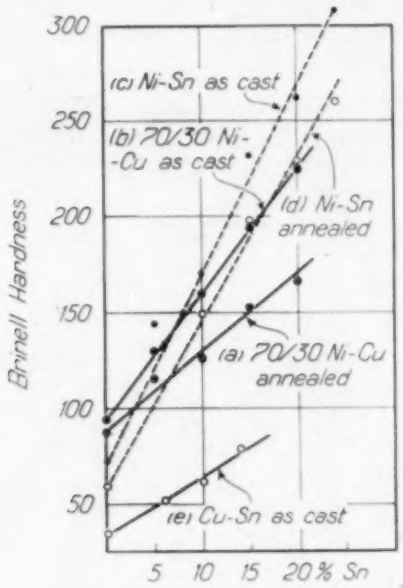


Fig. 2—Effect of Rising Additions of Tin on the Hardness of Nickel, 70/30 Nickel-Copper and Copper.

As was to be expected, the precipitation hardening effects increase progressively with rising tin concentrations, i.e., with increasing supersaturations of the 70/30 nickel-copper solid solution. The most suitable aging temperature for attaining the highest possible precipitation hardening effect is lowered with rising tin contents.

Fig. 6 gives the changes of hardness for the 20 per cent tin-bearing alloy aged in the temperature range of 400 to 550 degrees Cent. (750 to 1020 degrees Fahr.) for 300 hours. As is also observed with other precipitation hardening alloys, the maximum hardening effects become lower and lower with rising aging temperatures, which require shorter times for reaching the peak of the hardness/time curve. This is attributed to the fact that the velocity of grain growth of the precipitant becomes more pronounced while the number of nuclei is suppressed more and more.

Table IV presents at a glance the maximum hardening effects in relation to rising tin additions to the 70/30 nickel-copper base alloy. Column 5 gives the heat treatment applied to obtain these hardness

maxima. As can be seen, the annealing times have been extended beyond the 300-hour limit of Figs. 3, 4 and 5. The maximum hardness of 516 Brinell and the gain of 348 Brinell in the 20 per cent tin-containing alloy represents an imposing result for a nonferrous alloy.

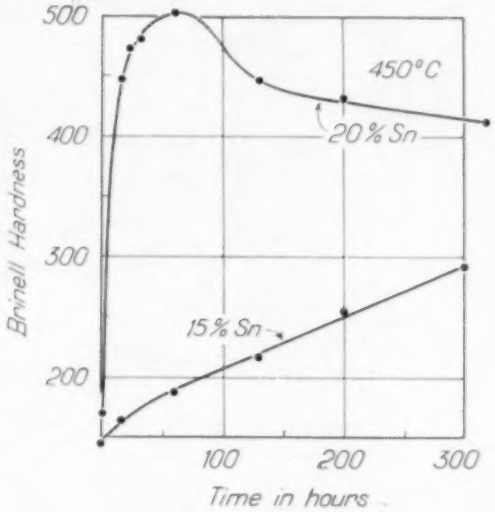


Fig. 3—Aging of Tin-Containing Nickel-Copper (Ratio 70/30) at 450 Degrees Cent. (840 Degrees Fahr.).

The actual possibilities of hardening the 5 per cent tin-bearing alloy have not been fully investigated yet, but it can be reasonably expected that the same conditions prevail in this alloy as in the binary nickel-tin alloy containing 5 per cent tin. For the latter alloy, aging treatments up to 2000 hours had to be applied for bringing

Table IV

Precipitation Hardening Effects Induced by Rising Additions of Tin to a 70/30 Nickel-Copper Base Alloy

	Brinell Hardness				
% Sn	As Quenched 1000° C.—30 min.	Fully Aged	Maximum Hardness Gain	Heat Treatment	Brinell Hardness As Cast
0	90	...	...	....	94
5	117	120	3	550° C.—614 hrs.	130
10	127	188	61	550° C.—614 hrs.	160
15	150	431	281	450° C.—700 hrs.	194
20	168	516	348	400° C.—150 hrs.	226

about maximum age-hardening (8). The conditions are rather peculiar in the 5 per cent tin alloy insofar as a very narrow useful temperature range for carrying out the hardening treatment is available. If too high a temperature is applied, the proportion of tin

which remains in solid solution owing to the curvature of the alpha-phase boundary line, and which thus does not participate in the precipitation hardening, becomes relatively large. This reduces the maximum precipitation hardening effects notably. On the other hand,

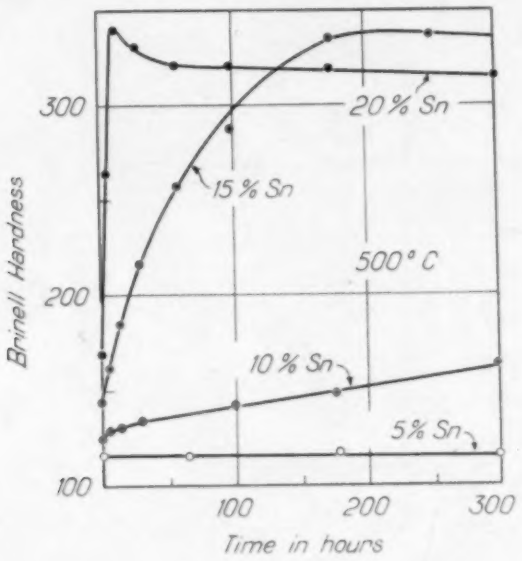


Fig. 4—Aging of Tin-Containing Nickel-Copper at 500 Degrees Cent. (930 Degrees Fahr.).

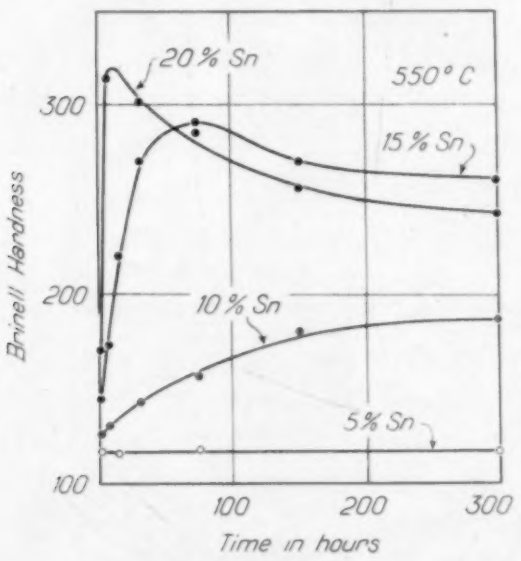


Fig. 5—Aging of Tin-Containing Nickel-Copper at 550 Degrees Cent. (1020 Degrees Fahr.).

the application of too low an aging temperature results in a "freezing in" of the alloy due to the slow mobility of the atoms in the space lattice of the alloy, which has a comparatively high melting point

Whether the retardation of the formation of nuclei of the precipitating phase (or "knots") represents a further contributing factor will be rather difficult to decide.

As is the case with binary nickel-tin alloys, the precipitating phase responsible for the aging effects in the face-centered, nickel-rich nickel-copper solutions down to 45 per cent nickel is the brittle, hexagonal, intermetallic compound Ni_3Sn (11). It is needless to say that, by additions of other elements partly soluble in the nickel-copper solid solution, the amounts of tin made available for the precipitation hardening can be increased. As the rate of precipitation hardening and optimum temperature of other age-harden-

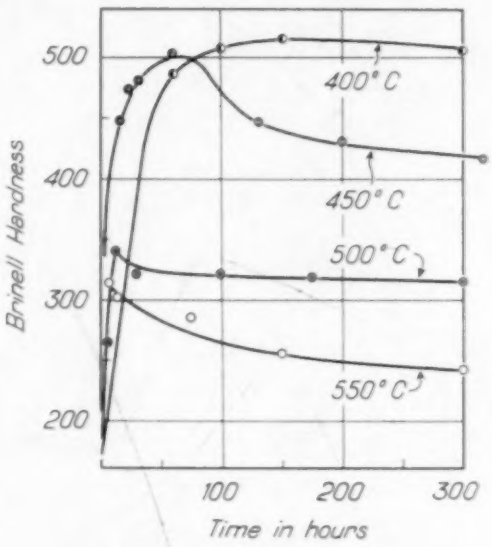


Fig. 6—Precipitation Hardening of a 56/24/20 Nickel-Copper-Tin Alloy in Relation to Aging Temperature and Time.

able Monel metals is different from the tin-containing alloys, a study of the Monel metal containing such two kinds of elements would be of both theoretical and practical interest.

Wrought Alloys

Plastic Deformation of Tin-bearing 70/30 Nickel-Copper—It is generally known that the plastic deformation of pure copper-tin bronzes becomes more and more difficult with rising tin concentrations, in particular above 12 per cent tin. About the same conditions hold for 70/30 nickel-copper alloyed with tin. A reduction of thickness of 40 per cent was carried out on a recrystallized 15 per cent tin-

containing specimen of relatively small height. As is the case with the tin-bronzes, the strain hardening effects on cold working become rather accentuated with increasing tin contents. Fig. 7 shows the interrelation between per cent reduction in cold rolling and strain hardening for plain 70/30 nickel-copper and for the 5 and 10 per cent tin-bearing alloy. Comparatively little further work hardening takes place in the 70/30 alloy after about 35 per cent reduction, while

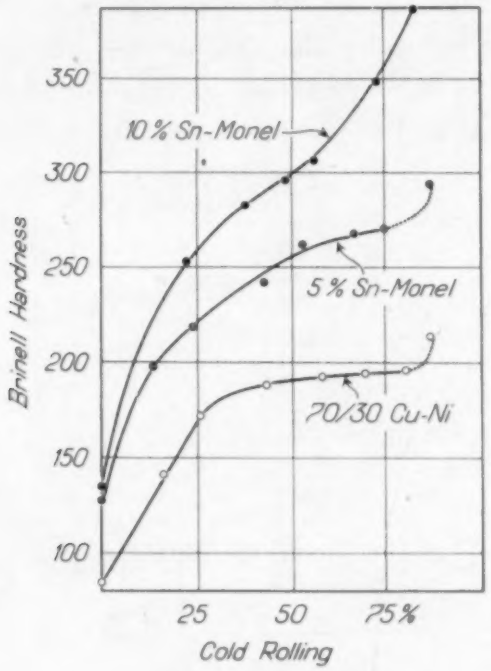


Fig. 7—Effect of Tin on the Work Hardening of 70/30 Nickel-Copper.

in the alloys containing tin, the strength continues to rise. This would necessitate more frequent intermediate annealings in commercial production. The abrupt hardness increase at "extreme" reductions may be due to the relative thinness of the samples and to the "anvil effect" of the hardness tester. However, attention has been called to a similar effect by Moore (31) who noticed an abrupt hardness increase in severely cold-worked copper.

From a scientific and technological point of view, the most important questions arising from the possibilities of aging cold-worked tin-bearing nickel-copper appear to be:

(1) Are the softening temperatures lower than the relatively high aging temperatures, thus leading to higher strength values by superimposition of strain hardening and precipitation hardening effects?

(2) Does the increase of the total lattice energy by cold working materially accelerate the relatively slow breakdown of the alpha-solid solution and does it lower the most suitable aging temperature?

Softening of 70/30 Nickel-Copper

The recovery of solid solution type alloys from cold working is apparently greatly affected by the presence of foreign elements. Softening of severely cold-worked copper and nickel of high purity was observed at temperatures as low as 80 (32) and 350 degrees Cent. (33-36) respectively. The relation between the temperature of hardness recovery and chemical composition of the binary system

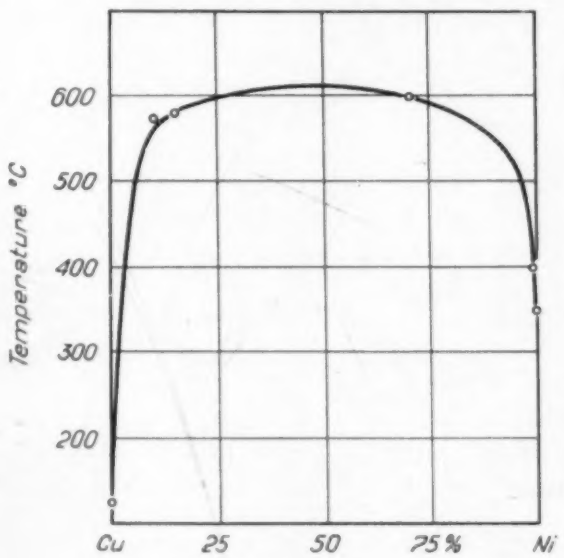


Fig. 8—Hardness Recovery of Cold-Worked Copper, Nickel-Copper Solid Solutions and Nickel.

copper-nickel yields a curve which is of the same type as that of electrical resistance, alloy hardness, thermo-power, endurance bending strength, etc., in binary systems built by a series of solid solutions with random atom distribution (see Fig. 8). The addition of the first few per cent of the second metal exerts a more or less pronounced influence upon these physical properties than larger additions. On the copper side, the softening temperatures (loss of 50 per cent of work hardness) of 10 and 15 per cent nickel alloy of technical purity was previously found at 575 and 580 degrees Cent. respectively (2). It appeared desirable to check on the softening

range of a copper-nickel alloy of higher nickel concentration, and to decide further whether the 70/30 nickel-copper alloy maintains its work hardness at temperatures reasonably higher than the precipitation hardening temperatures of the tin-containing 70/30 alloy as to warrant any aging tests in the cold-worked state.

The effect of rolling and annealing of pure 70/30 nickel-copper is shown in Fig. 9a-c. The three sections of the figure show respectively; a, the relation of strain hardening to the amount of plastic deformation; b, the relation of the recovery of hardness from cold work to annealing temperature and to amount of reduction in thickness, and c, the softening temperatures derived from the individual

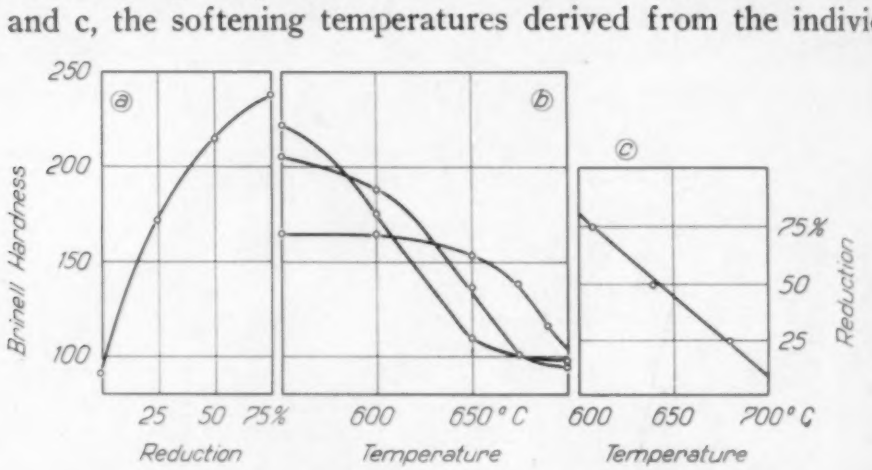


Fig. 9—Strain Hardening and Softening of Cold-Rolled 70/30 Nickel-Copper (Flats).

softening curves of section b. As the characteristic softening values, those temperatures have been taken at which a sample lost half of its maximum hardness.

According to Fig. 9, temperatures higher than 600 degrees Cent. (1290 degrees Fahr.) must be applied to soften the alloys during a 1-hour annealing to such an extent as to lose 50 per cent of the induced work hardening. At a reduction of 25 per cent, the recovery temperature is close to 680 degrees Cent. Since the softening temperatures of 70/30 nickel-copper are well above the optimum precipitation hardening temperatures of the tin-bearing alloys, it would appear that the strength of the latter could be raised by an aging in the cold-worked state.

Aging of Cold-Worked Tin-Bearing 70/30 Alloys

Solution annealed samples of the alloys containing 5 and 10 per cent tin were cold-rolled approximately 25, 50, 75 and 85 per cent and

aged for 1000 hours at 550 and 450 degrees Cent. (1020 and 840 degrees Fahr.). A 40 per cent cold-rolled sample of the 15 per cent tin alloy was aged at the same temperatures.

At 550 degrees Cent. (1020 degrees Fahr.), the first hardness test after 60 hours (Table V) shows that softening of the 5 per cent tin alloy had taken place. This becomes more and more pronounced with aging time. Even the least deformed sample lost its work hardness. After several hundred hours of additional aging treatment, an increase of hardness takes place, apparently through precipitation hardening. The maximum hardness, particularly of the more plastically deformed samples, exceeds that of the quenched 5 per cent

Table V

Hardness Changes of Cold-Rolled Tin-Bearing 70/30 Nickel-Copper During Aging at 550 Degrees Cent.

			Aging Time in Hours						
Alloy	Cold Work in %	Hardness as Rolled	60	200	460	575	700	850	1000
5% Tin	24	241	182	99	...	112	127	132	126
	53	253	193	110	109	125	136	139	125
	74.3	270	182	120	98	127	144	153	135
	86.5	288	180	86	90	127	141	156	144
10% Tin	22.5	256	110	120	150	172	208	206	190
	48.2	288	112	115	172	185	205	225	195
	72.3	369	110	117	181	200	216	216	195
	82	392	...	140	190	165	222	209	195

tin alloy in the fully aged state (Table IV), namely 156 Brinell versus 120 Brinell. The gain of some 36 Brinell units has, of course, no practical value, but it is of theoretical interest insofar as a mild superimposing of cold and age-hardening effects was obtained.

It is noteworthy that the cold-worked 10 per cent tin alloy softens at a faster rate than the 5 per cent tin alloy, indicating that rising additions of tin to 70/30 nickel-copper lower the temperatures at which the induced cold work hardness is released. According to Table V, not all of the strain hardening effect is abolished, so that the maximum hardness due to combined cold working and precipitation hardening exceeds somewhat the maximum hardness in the quenched 10 per cent tin alloy, i.e. 225 Brinell versus 188 Brinell.

One factor should not be overlooked, namely, the effect of time. The softening characteristics of the plain 70/30 nickel-copper alloy (see Fig. 9) were obtained on the basis of annealing times of only 60 minutes duration, while the aging experiments described above refer to heat treatments of several hundred hours. It is generally

known that the hardness recovery temperatures can be materially lowered by increasing the annealing times (35). It appears that both factors, the presence of tin and the slowness of the precipitation and the subsequent long aging times are responsible for the release of work hardness at 550 degrees Cent. (1020 degrees Fahr.) even in the least deformed samples.

It was expected that, by lowering the aging temperature to 450 degrees Cent. (840 degrees Fahr.), the release of the strain hardening effects would be avoided and that the precipitation hardening effects and work hardening could be superimposed. Table VI shows

Table VI

Hardness Changes of Cold-Rolled Tin-Bearing 70/30 Nickel-Copper During Aging at 450 Degrees Cent.

		Aging Time in Hours								
Alloy	Cold Work in %	Hardness as Rolled	50	97	150	210	300	500	686	825	1010
5% Tin	24	245	226	...	223	223	223	219	220	226	195
	53	253	228	242	238	234	233	228	219	244	205
	74.3	272	245	245	238	232	241	240	240	246	210
	86.5	290	243	272	260	248	238	244	245	238	225
10% Tin	22.5	256	233	240	245	252	252	255	245	250	230
	48.2	290	280	280	280	270	276	269	270	274	268
	72.3	335	311	298	276	276	269	260	274	274	260
	82	357	314	306	312	300	280	280	273	271	267

the variations of hardness in relation to aging time, and amount of plastic deformation of the alloys containing 5 and 10 per cent tin. In contradistinction to the aging behavior at 550 degrees Cent. (1020 degrees Fahr.), almost no softening takes place at 450 degrees Cent. (840 degrees Fahr.) in the early stages of the thermal treatment. The hardness of the 5 per cent tin alloy changes but little, a gradual softening taking place in the most deformed samples. The cold work hardness of the 5 and 10 per cent tin alloy materially exceeds the maximum precipitation hardening of the quenched alloy. But obviously no further gain in strength can be obtained by aging the 5 and 10 per cent tin-bearing alloys in the cold-worked state at 450 degress Cent. (840 degrees Fahr.).

An addition of precipitation hardness to cold work hardness was obtained by aging the 40 per cent cold-rolled sample of 15 per cent tin alloy at 400 degrees Cent. (750 degrees Fahr.) (see Fig. 10). The hardness of 294 Brinell induced by cold working was raised to 460 Brinell. This is about 30 Brinell higher than that of the quenched sample fully aged at 450 degrees Cent. (840 degrees Fahr.)

for 700 hours. This hardness maximum was attained in the cold-worked specimen in about the same time, but at a temperature 50 degrees lower. It thus appears that cold working has increased the rate of precipitation. At 455 degrees Cent. (850 degrees Fahr.) the release of strain hardening and the breakdown of the alpha solid solution take place simultaneously and the changes of hardness are not very conspicuous. A similar retardation of softening due to simultaneous precipitation hardening effects was for instance observed in brass containing small amounts of iron (37).

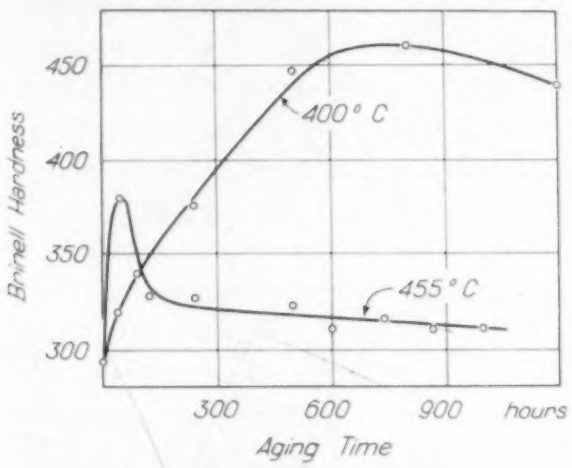


Fig. 10—Precipitation Hardening of a 59.5/25.5/15 Nickel-Copper-Tin Alloy Cold-Rolled 40 Per Cent.

Discussion

Among the precipitation hardening Monel metals, the aluminum-bearing alloys appear to have gained commercial importance. The foundry difficulties encountered with alloys high in aluminum are generally appreciated. The same objection holds—although to a far greater extent—for beryllium whose great affinity toward oxygen involves considerable loss in melting. Beryllium additions render the molten alloy rather viscous and sluggish and result in a pronounced tendency to form continuous oxide films, pipes and blow-holes in the casting (38). Another obstacle in the way of commercial success of beryllium-Monel is the rather high price of beryllium. The foundry and casting properties of silicon-Monel are rather good. However, this alloy is available only for casting purposes and the actual age-hardening effects are comparatively small. According to the writer's knowledge, little is known about titanium-Monel. Higher percentages of titanium are bound to introduce difficulties as is known

from experience with other nonferrous alloys. Kroll (39) considers 3 per cent titanium as the limit for melting in an open crucible and attributes the "thickening" of titanium-bearing melts to nitrogen absorption. The very moderate aging effects induced by indium in nickel-copper and the rarity of this metal seriously interfere with the commercial success of an indium-Monel metal.

In view of the above mentioned shortcomings of these modified, hardenable Monel metals, it was felt that the addition of a tin-bearing alloy to the family of age-hardening alloys having the nickel-copper ratio as in Monel metal offers definite commercial possibilities. The use of tin facilitates the foundry manipulations and the tin losses are relatively low. There are no objections to adding tin to the commercially available Monel metal instead of using a pure 70/30 nickel-copper base alloy. Owing to the considerable change of solubility of tin with temperature in 70/30 nickel-copper, maximum age-hardening of over 500 Brinell or a hardness increase of about 350 Brinell were obtained in quenched alloys of maximum supersaturation. In this respect the new tin-bearing alloys surpass all other precipitation hardening Monel metals reported so far. The relatively low hardness of the quenched alloys appears to be a valuable asset. Adding for instance 20 per cent tin raises the solution hardness to about the same extent as the addition of 1.5 per cent beryllium.

At tin concentrations of about 15 per cent, the alloys will probably be used mainly as castings. A shortcoming seems to be the relatively long annealing treatments necessary to produce maximum hardening. This feature is shared by the precipitation hardening binary nickel-tin alloys (8). However, few alloys are aged to their maximum hardness because ductility drops therewith to zero. An interesting feature is the improvement of the oxidation resistance of pure 70/30 nickel-copper with rising additions of tin. The silvery-white color of the 70/30 alloy is affected but little by alloying tin with it.

Summary

1. The effect of rising additions of tin on the precipitation hardening characteristics of a 70/30 nickel-copper base alloy was investigated. A maximum hardness of over 500 Brinell, or a gain of about 350 Brinell over the annealed state, was observed on the alloy containing 20 per cent tin.

2. A superimposing of precipitation hardening and work harden-

ing was obtained only in exceptional cases because tin lowers the hardness recovery temperatures of pure 70/30 nickel-copper and because relatively long aging times are required for nickel-copper alloys which are high in nickel and rendered subject to precipitation hardening by the addition of tin.

3. Alloys containing 5 and 10 per cent tin were cold-rolled up to 90 per cent. Moderate plastic deformation at room temperature was possible with samples containing 15 per cent tin.

4. Rising additions of tin progressively increase the strain hardening effects of quenched 70/30 nickel-copper alloys, and the resistance toward scaling.

Acknowledgments

The author wishes to express his indebtedness to Dr. C. L. Mantell, technical director of Wilbur B. Driver Company, and to Mr. Fred P. Peters, formerly chief chemist, Wilbur B. Driver Company, now assistant editor of "Metals and Alloys," for their helpful criticism and suggestions in the preparation of this paper. Most of the experimental work reported above was carried out in 1934 and 1935 in the Metallurgical Research Laboratories at Columbia University.

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INFLUENCE OF CHROMIUM, SILICON AND ALUMINUM ON THE OXIDATION RESISTANCE OF INTERMEDIATE ALLOY STEELS

By A. E. White, C. L. Clark and C. H. McCollam

Abstract

This paper presents the results of an investigation undertaken to determine the influence of chromium, silicon and aluminum on the oxidation resistance of intermediate alloy steels. It is shown that through the proper combination of these elements a high degree of oxidation resistance can be obtained at temperatures as high as 1500 to 1750 degrees Fahr. (815 to 955 degrees Cent.).

Both silicon and aluminum were found to be more effective than chromium in imparting oxidation resistance provided chromium was likewise present. In fact the experimental findings indicate silicon to be seven times and aluminum four times as effective as chromium under the given test conditions.

Chemical and microscopic examination of certain of the scaled specimens substantiates the theory that the increased oxidation resistance produced by the addition of these elements is caused by their increased concentration as oxides in the inner scale layer which becomes impermeable and adherent to the surface of the steel.

Introduction

CONSIDERABLE effort has been extended during the past ten years to the development of steels for high temperature service. Much of this work has been directed towards improvement of strength, and especially creep resistance, and proper attention has not always been given to the fact that strength, in itself, is not sufficient for satisfactory high temperature service. In other words, if the surface of the steel is not stable under the given operating conditions

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then the cross sectional area will be decreased, the unit stress increased and the expected life shortened.

It so happens that chromium, which is one of the elements commonly added for the purpose of improving the strength, likewise increases the surface stability. Small additions of this element have been found to impart an effective resistance against certain types of corrosion, especially that encountered in certain crude oils. However satisfactory oxidation resistance at temperatures above 1200 degrees Fahr. (650 degrees Cent.) requires chromium contents in excess of 6 per cent, with consequent influence on the physical properties and the cost of the material.

It is generally agreed that improved resistance to oxidation can be obtained by the addition of those elements which have a greater affinity for oxygen than iron and whose oxides form a dense and firmly adhering scale at the surface of the steel. Two elements which meet these qualifications, in addition to chromium, are silicon and aluminum. These two elements have not been used to a wide extent for improving the oxidation resistance largely because of misconceptions with respect to their influence on the physical characteristics of the resulting steels.

Preliminary work on steels containing some or all of these three elements indicated each might be more effective in the presence of certain amounts of the other two. Accordingly it was believed advisable to investigate a rather complete series of these steels.

Steels Investigated

The steels necessary for this investigation were furnished by The Timken Steel and Tube Division of The Timken Roller Bearing Company. They were in the form of hot-rolled 1-inch bars and were from electric furnace commercial heats. The chemical composition of these steels, as well as the heat treatment to which they were subjected and the resulting Brinell hardness, is given in Table I. Their room temperature tensile properties after the same heat treatment are given in Table II and all are seen to possess a good combination of strength and ductility.

The steels may be classified into five groups. The first group of four steels is of the silicon-chromium-molybdenum type and the individual steels differ mainly in that the chromium is varied from 1.30 to 4.83 per cent. The second group differs from the first only in that

aluminum is present in an amount of approximately 0.55 per cent. The 5-2-3 steel differs from the highest chromium-bearing steel of the second group in that it contains a greater silicon and molybdenum

Table I
Chemical Composition, Heat Treatment and Brinell Hardness of Steels Subjected to Oxidation Tests

Steel Designation	Heat Treatment Deg. Fahr.	Chemical Composition, Per Cent C	Mn	P	S	Si	Cr	Mo	Al	Brinell Hardness
Si-Cr-Mo 1	Ann. 1550	0.15	0.42	0.017	0.016	1.37	1.30	0.54	...	156
Si-Cr-Mo 2	Ann. 1550	0.09	0.41	0.010	0.017	1.32	2.06	0.51	...	146
Si-Cr-Mo 3	Ann. 1550	0.12	0.43	0.008	0.014	1.57	3.26	0.50	...	159
Si-Cr-Mo 5	Ann. 1550	0.10	0.38	0.009	0.016	1.55	4.83	0.51	...	156
Al-Cr-Si 1	Ann. 1650	0.17	0.24	0.009	0.010	1.22	1.06	0.51	0.57	156
Al-Cr-Si 2	Ann. 1650	0.16	0.25	0.009	0.013	1.34	1.94	0.48	0.53	149
Al-Cr-Si 3	Ann. 1650	0.18	0.30	0.013	0.012	1.27	3.10	0.59	0.57	156
Al-Cr-Si 5	Ann. 1650	0.10	0.29	0.012	0.010	1.36	4.96	0.60	0.54	149
5-2-3	Ann. 1550	0.09	0.42	0.011	0.008	2.26	5.10	3.45	0.55	229
12 Cr	Ann.	0.10	0.38	0.025	0.022	0.35	12.19	0.27	...	165
17 Cr	Ann.	0.10	0.36	0.029	0.010	0.85	17.07	0.03	...	161
18 Cr-8 Ni	W.Q. 2000	0.06	0.50	0.008	0.008	0.61	17.75		9.25 Ni	137

Note: Both the oxidation and tensile specimens were taken from hot-rolled 1-inch bars which were given the designated heat treatment prior to machining. All the bars were from commercial electric furnace heats of steel.

Table II
Room Temperature Tensile Properties of Steels Subjected to Oxidation Tests

Steel Designation	Tensile Strength Lbs. Per Sq. In.	Yield Stress Lbs. Per Sq. In. 0.1 Per Cent	0.2 Per Cent	Proportional Limit Lbs. Per Sq. In.	Elongation Per Cent in 2 In.	Reduction of Area Per Cent
Si-Cr-Mo 1	80,400	50,400	52,100	33,250	34.0	66.7
Si-Cr-Mo 2	75,100	48,750	49,600	32,500	37.0	73.3
Si-Cr-Mo 3	84,900	46,750	48,100	24,400	35.5	73.9
Si-Cr-Mo 5	82,100	45,000	45,000	36,250	38.75	76.2
Al-Cr-Si 1	80,300	37,500	39,250	25,000	35.0	69.1
Al-Cr-Si 2	71,600	46,250	47,000	31,500	38.5	69.2
Al-Cr-Si 3	72,000	39,600	40,350	21,800	40.25	72.3
Al-Cr-Si 5	69,600	38,000	39,750	26,000	41.0	76.3
5-2-3	101,900	62,000	64,000	50,000	23.5	49.8
12 Cr	84,300	56,000	60,000	32,500	32.0	73.6
17 Cr	80,000	47,000	49,250	28,750	33.5	67.6
18 Cr-8 Ni	85,200	26,500	27,900	12,500	61.5	74.4

Note: Each value is the average of duplicate tests in good agreement.

content. The fourth group consists of two chromium steels, containing 12 and 17 per cent of this element, while the last is the 18-8 steel which, together with the two straight chromium steels, is included to

serve as a yardstick in evaluating the oxidation resistance of the remaining steels.

All of the steels do therefore contain chromium and, with the exception of the 12 and 17 per cent chromium steels and the 18-8 alloy, possess silicon in excess of 1.0 per cent. Since the carbon and manganese contents are approximately the same the results obtained should indicate the influence of chromium, silicon and aluminum on the resulting oxidation resistance.

Procedure

The tests for determining the relative oxidation resistance of these steels, based on weight loss, were conducted at temperatures of 1250, 1400, 1500 and 1750 degrees Fahr. (675, 760, 815 and 955 degrees Cent.). These tests were continued for 1000 hours with one set of the specimens being heated continuously and the other intermittently. In the intermittent series the specimens were air-cooled at weekly intervals but the total time at temperature was again 1000 hours.

The specimens for this phase of the investigation were cylindrical, being ¾ inch in diameter by ½ inch in length, and all tests were conducted in triplicate. Laboratory type electric-muffle furnaces were employed and all the tests of each type for each temperature were conducted simultaneously. That is, 36 specimens were used and these were distributed uniformly over the length of the furnace. Each furnace was previously calibrated to insure uniformity of temperature distribution.

No attempts were made in the present investigation to control the amount, or composition, of the air entering the furnace. The results for each steel are therefore comparative and not quantitative under absolutely known conditions. However, as all of the specimens were tested simultaneously, the influence of chemical composition on the oxidation resistance of the steels should be clearly demonstrated.

Upon completion of the tests, the specimens were air-cooled and as much as possible of the scaled layer removed mechanically. The remaining scale was then removed in an electrolytic stripping cell in which the scale is loosened by the evolution of the hydrogen generated on the specimen.

Work was likewise conducted on certain of the steels for the purpose of studying the scale structure microscopically and de-

termining its chemical composition. For this phase of the investigation the steels were exposed at 1500 degrees Fahr. (815 degrees Cent.) in air for 350 hours. In these tests the same type specimen was used for the metallographic examination as in the regular oxidation tests. Samples prepared for chemical analysis, however, were cylinders, ¾-inch round by 6 inches in length. After the above exposure period, the oxide coat was removed mechanically in two portions, designated as the inner and outer layers, after which two cuts, each 0.002-inch thick, were machined from the steel surface of the specimens. Chemical analyses obtained on these specimens are presented later.

Results

The results obtained from the 1000-hour oxidation tests at temperatures of 1250, 1400, 1500 and 1750 degrees Fahr. (675, 760, 815, and 955 degrees Cent.) are summarized in Table III and shown graphically in Figs. 1 and 2. These two figures differ only in that the first presents the results from the continuous heating tests and the second, those from the intermittent tests.

Table III

Comparative Oxidation Resistance of Indicated Steels at Designated Temperatures Specimen Heated Either Continuously or Intermittently* for 1000 Hours as Indicated

Steel Designation	1250° F.		1400° F.		1500° F.		1750° F.	
	Cont.	Int.	Cont.	Int.	Cont.	Int.	Cont.	Int.
	Loss in Weight, Grams, per Sq. In. of Original Surface							
Si-Cr-Mo 1	1.32	0.91	1.78	1.25	2.68	4.27	9.68	9.03
Si-Cr-Mo 2	1.20	0.71	1.40	0.98	2.40	4.37	9.65	8.48
Si-Cr-Mo 3	0.33	0.16	0.67	0.24	1.21	3.20	9.25	8.23
Si-Cr-Mo 5	0.02	0.05	0.05	0.04	0.04	1.88	6.79	8.21
Al-Cr-Si 1	1.02	0.84	2.06	1.19	2.83	5.13	10.53	9.24
Al-Cr-Si 2	0.74	0.46	1.16	0.86	2.32	4.94	10.72	8.35
Al-Cr-Si 3	0.27	0.15	0.28	0.11	2.15	4.72	9.08	7.60
Al-Cr-Si 5	0.02	0.02	0.11	0.03	0.03	0.28	2.08	1.97
5-2-3	0.01	0.02	0.05	0.01	0.01	0.02	0.01	0.05
12 Cr	0.01	0.03	0.05	0.02	1.18	0.37	7.35	11.01
17 Cr	0.01	0.04	0.03	0.01	0.03	0.03	0.48	0.94
18-8	0.01	0.04	0.04	0.01	0.02	0.15	0.19	0.80

*In the intermittent tests the specimens were air-cooled at weekly intervals. Total time at temperature was, however, 1000 hours.

Note: Each reported value is the average of three tests.

Continuous Heating Tests—First considering the four silicon-chromium-molybdenum steels it is evident that the oxidation resist-

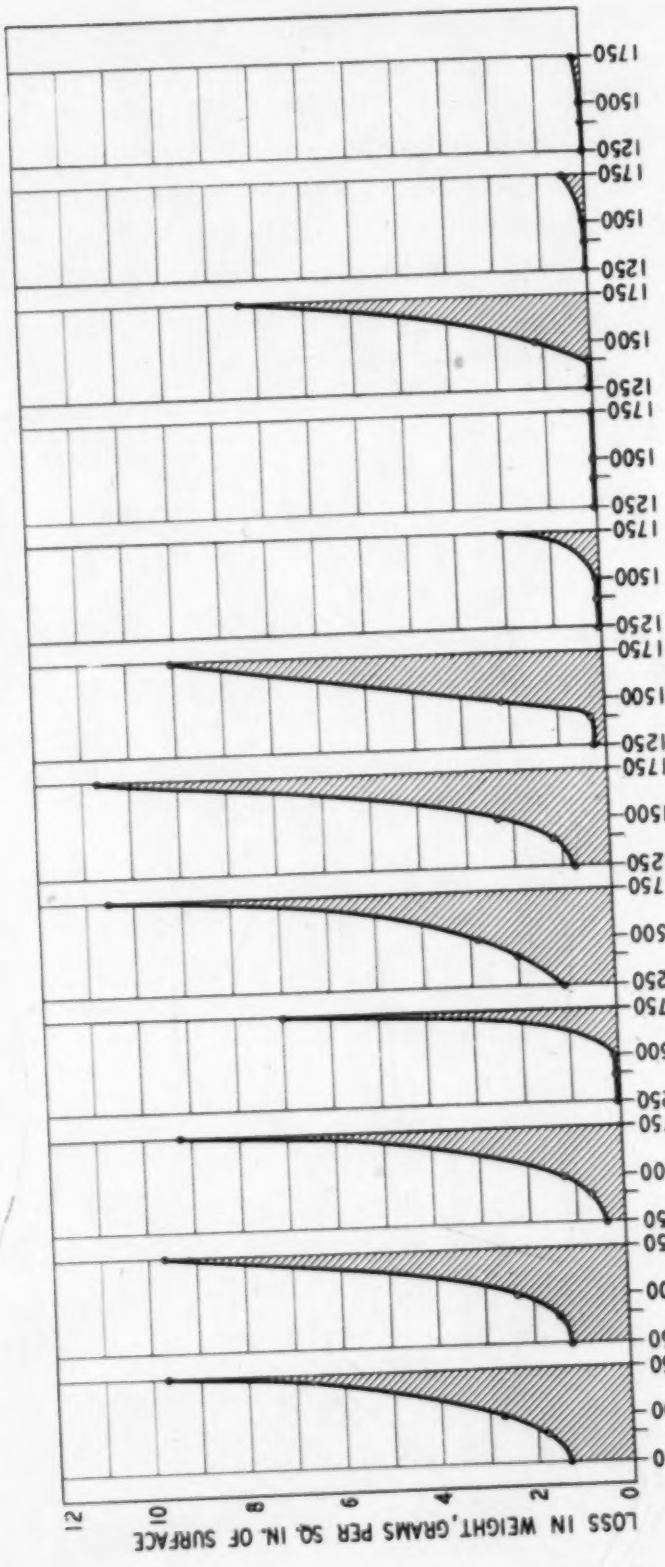


Fig. 1—Comparative Oxidation Resistance of Indicated Steels at Designated Temperature. 1000 Hours Continuous Heating Tests.

ance is improved as the chromium content is increased. Only a slight improvement is obtained as the chromium is raised from 1.30 to 2.0 per cent, but a further increase to 3.26 per cent results in a marked improvement in the oxidation resistance at 1250, 1400 and 1500 degrees Fahr. (675, 760, 815 degrees Cent.) but not at 1750 degrees Fahr. (955 degrees Cent.). When the chromium content is 4.83 per cent the steel has a very high resistance to oxidation at temperatures up to and including 1500 degrees Fahr. (815 degrees Cent.). At 1750 degrees Fahr. (955 degrees Cent.), however, this steel scales rather badly although even at this high temperature it is superior to the other three steels of this group. It should be noted that at 1500 degrees Fahr. (815 degrees Cent.) this higher chromium steel possesses an oxidation resistance comparable to that of the 17 per cent chromium and 18-8 steels and is superior to the 12 per cent chromium steel.

The aluminum-chromium-silicon-molybdenum steels behave in a similar manner to the four steels of the preceding group. That is, a slight improvement is obtained in the oxidation resistance at the three lower temperatures as the chromium is varied from 1.06 to 1.94 per cent, with a more marked improvement resulting as the chromium is further increased to 3.10 per cent. This latter steel possesses very good oxidation resistance at 1400 degrees Fahr. (760 degrees Cent.). With a further increase in the chromium content to 4.96 per cent, the oxidation resistance at 1500 degrees Fahr. (815 degrees Cent.) is very good, being comparable to that of the 17 per cent chromium and the 18-8 steels. A vast improvement has likewise resulted in the oxidation resistance at 1750 degrees Fahr. (955 degrees Cent.) although at this temperature the resistance is somewhat inferior to that of the higher chromium and the austenitic steels.

If the silicon content of the higher chromium steel of the aluminum-chromium-silicon-molybdenum group, is raised from 1.36 to 2.26 per cent, as in Steel 5-2-3, then a very high resistance to oxidation is obtained at all temperatures investigated. In fact this steel is superior in this respect to the 17 per cent chromium and the 18-8 steels. It is true that this steel also contains 3.45 per cent molybdenum but it is believed that the outstanding oxidation resistance is a result of the combination of silicon, chromium and aluminum.

Both the 12 and 17 per cent chromium steels exhibit a good resistance to oxidation at 1250 and 1400 degrees Fahr. (675 and 760

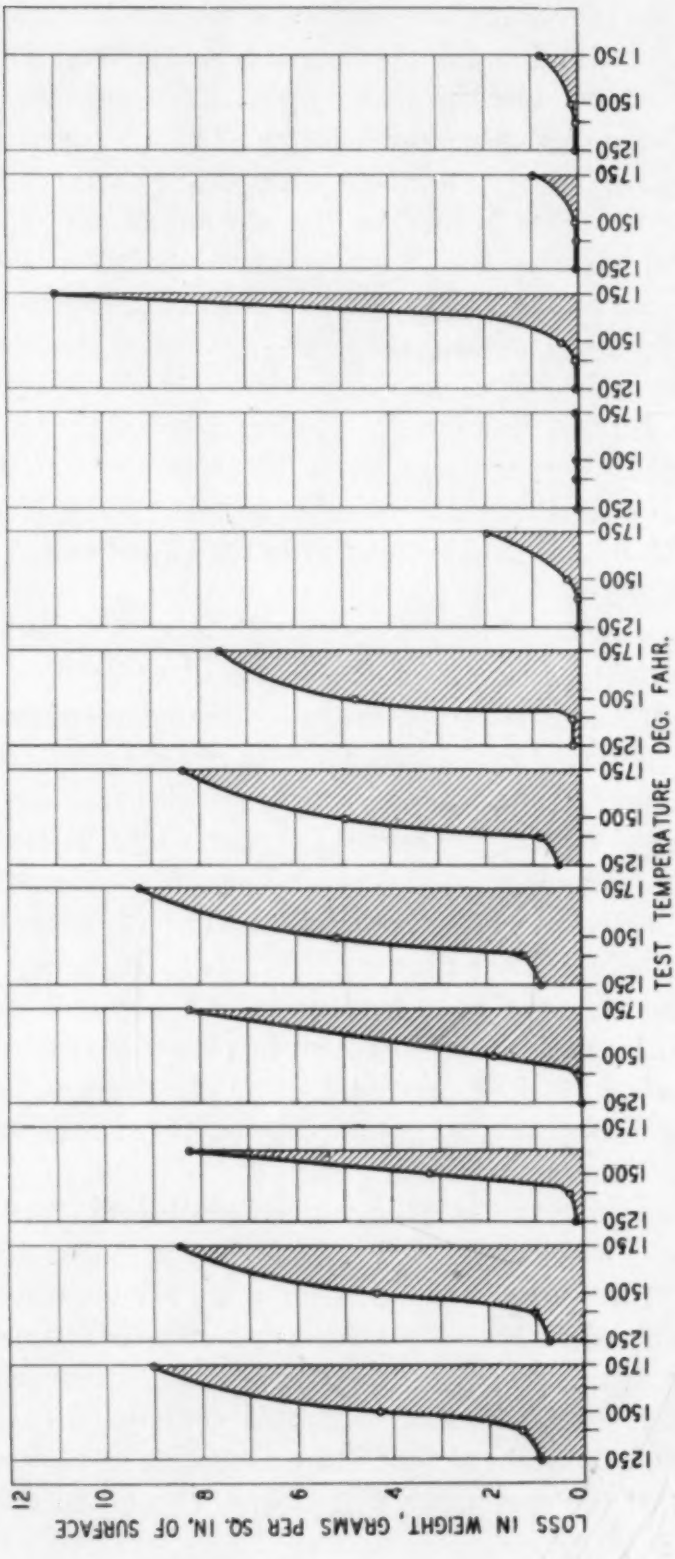


Fig. 2—Comparative Oxidation Resistance of Indicated Steels at Designated Temperature. 1000 Hours Intermittent Heating Tests.

degrees Cent.). At the higher temperatures the resistance of the lower chromium steel decreases at a rapid rate. On the other hand, the resistance of the 17 per cent chromium steel is good at both 1500 and 1750 degrees Fahr. (815 and 955 degrees Cent.).

Likewise the austenitic 18 per cent chromium-8 per cent nickel steel possesses good oxidation resistance at each of the temperatures considered.

Intermittent Heating Tests—The results obtained from the intermittent tests exhibit the same general trend as those from the continuous tests. At the two lower temperatures, however, the intermittent test gave somewhat lower scaling losses in nearly every case while at 1500 degrees Fahr. (815 degrees Cent.) the reverse was true. At 1750 degrees Fahr. (955 degrees Cent.) the differences were not consistent but for those steels which did possess the greatest resistance to oxidation at this temperature the intermittent test gave the larger loss.

In comparing these results it should be realized that the size and shape of the specimen was such that thermal stresses would be at a minimum. Mechanical stresses were likewise absent and thus the tendency of the scale to crack or spall from these causes was small, especially at the lower temperatures. This probably accounts for the increased oxidation resistance obtained at 1250 and 1400 degrees Fahr. (675 and 760 degrees Cent.) from the intermittent oxidation tests.

On the other hand 1500 degrees Fahr. (815 degrees Cent.) was above, or well within, the thermal critical range of the majority of steels considered. It is entirely possible therefore that the volume change, due to the transformation of the steel, caused some cracking of the scale on each heating and cooling cycle of the intermittent test and thus the scale loss was greater than in the continuous test. This belief is somewhat substantiated by certain of the curves of Fig. 2 which indicate that the increase in scaling rate between 1400 and 1500 degrees Fahr. (760 and 815 degrees Cent.) is greater than that between 1500 and 1750 degrees Fahr. (815 and 955 degrees Cent.). Such a condition was not found in any of the continuous tests or in the intermittent tests on these steels which either did not possess a definite critical range or in which this range was very high.

In many cases at 1750 degrees Fahr. (955 degrees Cent.) the nature of the scale produced was such that it offered little protection to further oxidation and, accordingly, the results were not greatly

influenced by the two types of tests. With the steels which did possess a high degree of oxidation resistance at this temperature, the thermal stresses caused by air cooling from so high a temperature may have been sufficient to cause slight cracking of the protective scale layer and thus cause the intermittent test to give the somewhat greater losses.

The conclusions to be drawn from the two types of tests are, however, the same, for in both cases a very high degree of oxidation resistance was obtained through the proper combination of chromium and silicon or of chromium, silicon and aluminum.

Discussion of Results

The results obtained show that, in the presence of a suitable amount of chromium, both silicon and aluminum are more effective than chromium alone in imparting a high degree of oxidation resistance. If this were not true then the Si-Cr-Mo 5 steel, which has a combined chromium plus silicon content of 6.38 per cent as well as the Al-Cr-Si 5 steel, which has a total aluminum plus silicon plus chromium content of 6.86 per cent, would both be less resistant to oxidation than the 12 per cent chromium steel. The experimental findings, however, definitely indicate the 12 per cent chromium steel to be inferior at the higher temperatures.

Relative Influence of Chromium, Silicon and Aluminum—In an attempt to properly evaluate the influence of silicon and aluminum on the oxidation resistance of these chromium-bearing steels various multiplying factors were used and it was found that the best relationship resulted when seven times the silicon and four times the aluminum content were used together with the chromium content. The resulting relationship at each of the four test temperatures is shown in Fig. 3. In other words, for these particular steels under the given test conditions and in the presence of chromium, silicon is seven times as effective as chromium in imparting oxidation resistance while aluminum is four times as effective.

It is not intended that this be considered as an absolute relationship for at each of the temperatures certain of the experimental results do not fall exactly on the curve. On the basis of this relationship, however, a step diagram does result, which is typical of the influence of varying chromium content on the oxidation resistance, and furthermore the results obtained from both the straight 12 and

17 per cent chromium steels are definitely correlated with those from the lower alloyed steels.

It should be further emphasized that, in the absence of chromium, neither silicon nor aluminum is as effective in improving the oxidation resistance as would be indicated by the above relationship.

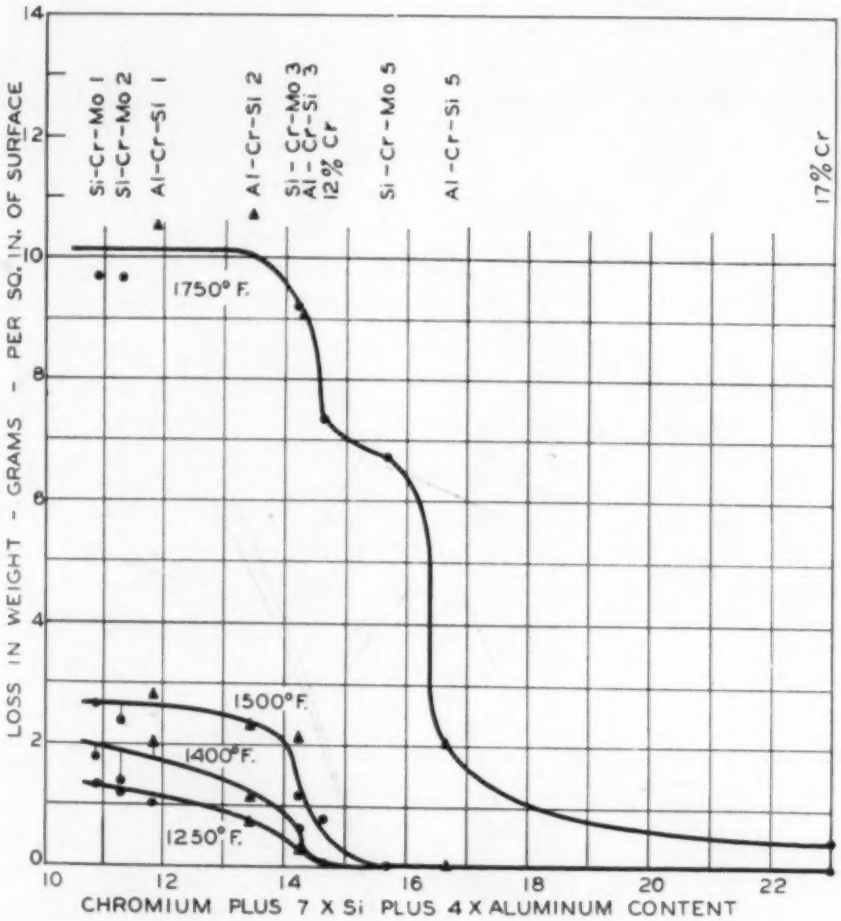


Fig. 3—Relationship Between Oxidation Resistance and Chromium Plus 7 Times Silicon Plus 4 Times Aluminum Content.

While there is no question but what increased silicon content does improve the oxidation resistance of chromium-free steels, the improvement is not as pronounced as when chromium is present. This point is illustrated by certain of the polished oxidation specimens of Fig. 4, which were prepared for the second phase of this investigation to be discussed later. Specimens A and D are both of the 0.50 per cent molybdenum type and differ only in the amount of silicon contained, the actual silicon content being 0.25 and 1.35 per cent, respectively. While both specimens were rather severely scaled at

1500 degrees Fahr. (815 degrees Cent.) the attack was the more pronounced on the lower silicon steel.

The remaining four specimens of Fig. 4 are included to show the influence of increasing chromium, both in the presence of low

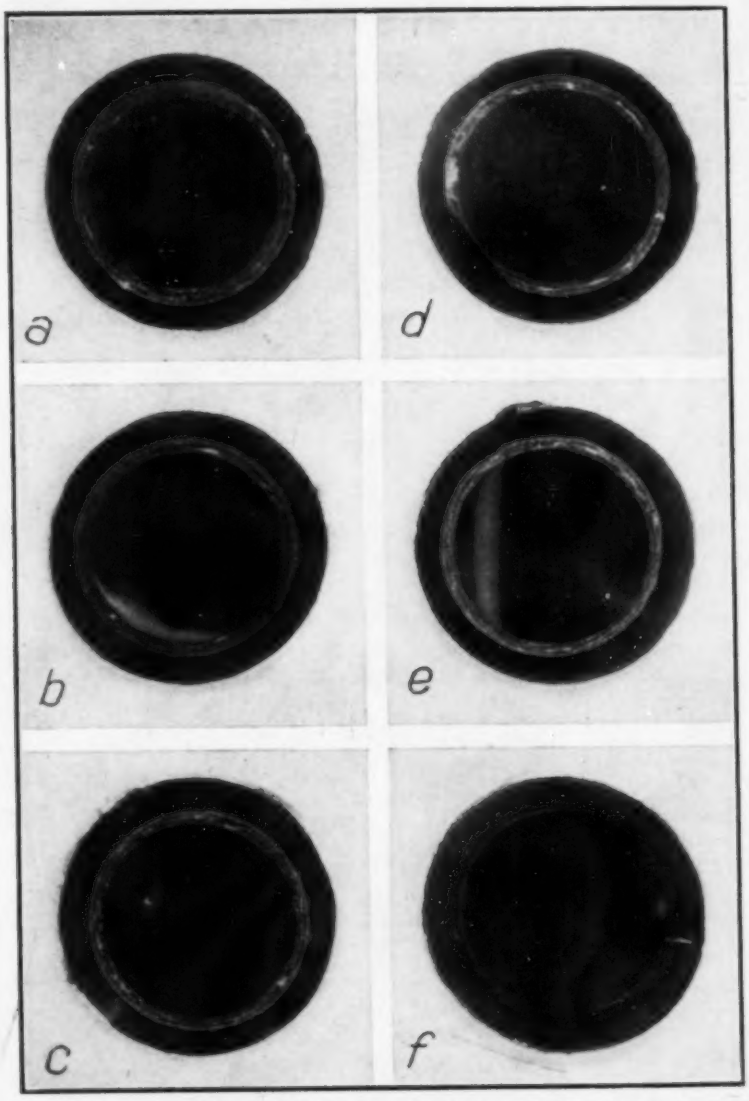


Fig. 4—Photograph of Typical Polished Oxidized Specimens After 350 Hours at 1500 Degrees Fahr.
Fig. A—0.52 Mo, 0.25 Si.
Fig. B—2.08 Cr, 0.50 Mo, 0.42 Si.
Fig. C—5.09 Cr, 0.55 Mo, 0.18 Si.
Fig. D—0.50 Mo, 1.35 Si.
Fig. E—2.06 Cr, 0.51 Mo, 1.32 Si.
Fig. F—4.83 Cr, 0.51 Mo, 1.55 Si.
Note: Specimens mounted in bakelite prior to polishing. Outer ring is the bakelite, center section is the steel and the intermediate layer is the scaled surface.

and high silicon, on the amount of scale produced. In the presence of 2.0 per cent chromium the amount of scaling is appreciably re-

duced by the addition of approximately 1.5 per cent silicon while with 5.0 per cent chromium this same amount of silicon prevents the formation of a visible layer of scale.

No steels were considered in which aluminum was present with a low silicon content and it is thus difficult to ascertain the exact influence of aluminum alone on the oxidation resistance. The relationship shown in Fig. 3 indicates silicon to be more effective than aluminum in this respect. This might not be true, however, if aluminum were present in amounts greater than 0.50 per cent. The presence of even this amount of aluminum, however, greatly improved the oxidation resistance at 1750 degrees Fahr. (955 degrees Cent.) of the Si-Cr-Mo 5 type steel. In the presence of lower amounts of chromium, however, its addition was not as beneficial.

Mechanism of Oxidation—It is generally assumed that the beneficial action of certain alloying elements in improving the oxidation resistance of steel is due to the fact that they have a greater affinity for oxygen than has the iron, and therefore they are preferentially oxidized. It is further assumed that the oxide layer thus produced is dense, impermeable and that it adheres firmly to the surface of the steel. As recently stated by Houdremont and Bandel[1] the maintenance of this protective oxide layer depends on a sufficient supply of the effective alloying elements diffusing to the surface so that the oxygen, penetrating through the protective layer, will be entirely consumed.

In the steels considered in this investigation chromium, silicon and aluminum all oxidize before iron and thus they fulfill at least one of the requirements for increased protection against oxidation. If diffusion is a deciding factor then silicon and aluminum should be more effective than chromium since they can be more readily diffused in steel. The addition of chromium, by itself, produces a dense and tightly adhering scale under certain oxidizing conditions and there are indications that this effect is intensified by the additions of silicon and aluminum.

In an effort to determine the behavior of certain alloying elements under oxidizing conditions, a series of chemical analyses, as well as metallographic examinations, were made on the steels illustrated in Fig. 4. These steels are of the 0.50 per cent molybdenum, the 2 per cent chromium + 0.50 per cent molybdenum, and the 4-6

[1] "Processes of Attack of Hot Gases on Heat-Resisting Steels," *Arch. Eisenhüttenw.* Vol. 11, 1937, p. 131-8.



Fig. 5—Influence of Increased Silicon Content on the Surface of 0.50 Mo Steel After 350 Hours at 1500 Degrees Fahr.—× 100.
Fig. 5a—0.52 Mo, 0.25 Si.
Fig. 5b—0.52 Mo, 1.35 Si.

chromium + molybdenum types and each group contains two different silicon contents, one below 0.50 per cent and the other of the order of 1.50 per cent. The results obtained from the chemical

analyses are given in Table IV while the microstructures are given in Figs. 5, 6 and 7.

The specimens were subjected to a temperature of 1500 degrees Fahr. (815 degrees Cent.) in air for 350 hours. The oxide layers thus produced were carefully removed and with one exception were divided into portions representing the inner and outer layers. The single exception was Si-Cr-Mo 5 steel which produced so thin an oxide layer that no sample could be obtained.

In addition to the scale layers, samples were taken from the steel surface after oxide removal by machining two cuts each 0.002-inch thick from the surface. These turnings are designated as outer and inner. It is probable that some oxide was inadvertently included in the outer steel cut.

Table IV

Chemical Analysis of Scaled Layer Produced During 350 Hours Heating at 1500° F.

Type Steel	Position of Sample	Chemical Composition, Per Cent							
		Cr	Cr_2O_3	Si	SiO_2	Mo	MoO_3	Cu	CuO
0.50 Mo	Outer Scale	Nil	Nil	0.09	0.19	0.22	0.33	Nil	Nil
	Inner Scale	0.10	0.14	0.43	0.92	0.67	1.01	0.08	0.10
	1st–0.002″ Cut	0.07	....	0.27	....	0.47	....	0.48	....
	2nd–0.002″ Cut	0.08	....	0.29	....	0.51	....	0.19	....
	Base Steel	0.07	....	0.25	....	0.52	....	0.17	....
0.50 Mo + 1.35 Si	Outer Scale	0.03	0.04	0.61	1.31	0.26	0.39	Nil	Nil
	Inner Scale	0.10	0.14	2.04	4.37	0.85	1.27	Nil	Nil
	1st–0.002″ Cut	0.07	....	1.27	....	0.49	....	0.32	....
	2nd–0.002″ Cut	0.07	....	1.33	....	0.54	....	0.17	....
	Base Steel	0.07	....	1.35	....	0.50	....	0.12	....
2 Cr + Mo	Outer Scale	0.51	0.74	0.12	0.26	0.16	0.24	Nil	Nil
	Inner Scale	3.13	4.57	0.64	1.37	0.81	1.21	Nil	Nil
	1st–0.002″ Cut	1.98	....	0.45	....	0.50	....	0.54	....
	2nd–0.002″ Cut	2.06	....	0.44	....	0.54	....	0.26	....
	Base Steel	2.08	....	0.42	....	0.50	....	0.06	....
2 Cr + Mo + 1.32 Si	Outer Scale	0.14	0.20	0.09	0.20	0.03	0.05	Nil	Nil
	Inner Scale	3.03	4.43	1.83	3.92	0.71	1.07	Nil	Nil
	1st–0.002″ Cut	1.95	....	1.31	....	0.52	....	0.21	....
	2nd–0.002″ Cut	2.07	....	1.34	....	0.50	....	0.17	....
	Base Steel	2.06	....	1.32	....	0.51	....	0.06	....
4-6 Cr + Mo	Outer Scale	0.09	0.13	0.01	0.02	Nil	Nil	Nil	Nil
	Inner Scale	7.42	10.85	0.23	0.49	0.76	1.14	Nil	Nil
	1st–0.002″ Cut	4.89	....	0.28	....	0.54	....	0.24	....
	2nd–0.002″ Cut	5.02	....	0.26	....	0.53	....	0.15	....
	Base Steel	5.09	....	0.18	....	0.55	....	0.09	....
4-6 Cr + Mo + 1.55 Si	Outer Scale	No Visible Layer Produced*							
	Inner Scale	No Visible Layer Produced*							
	1st–0.002″ Cut	4.45	....	1.51	....	0.49	....	0.06	....
	2nd–0.002″ Cut	4.55	....	1.64	....	0.47	....	0.06	....
	Base Steel	4.83	....	1.55	....	0.51	....	0.07	....

*Surface of the specimen was slightly tarnished.

From the results given in Table IV it is evident that a concentration of certain of the alloying elements, especially chromium, silicon

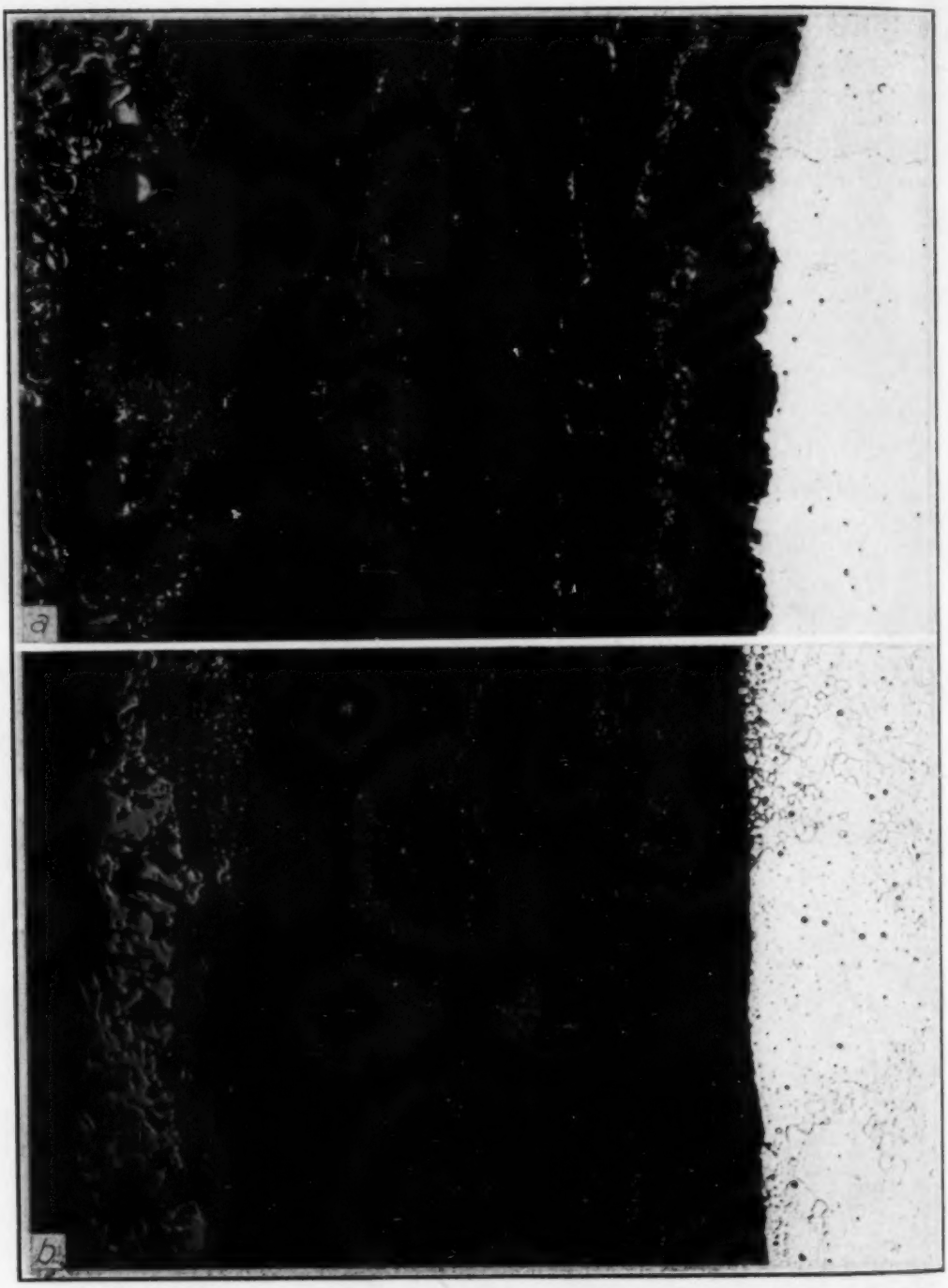


Fig. 6—Influence of Increased Silicon Content on the Surface of 2.0 Cr + 0.50 Mo Steel After 350 Hours at 1500 Degrees Fahr.—× 100.
Fig. 6a—2.08 Cr, 0.50 Mo, 0.42 Si.
Fig. 6b—2.06 Cr, 0.51 Mo, 1.32 Si.

and molybdenum, has occurred in the inner scale layer. The extent of this increase can be more readily seen from the values of Table V which set forth the ratio of the amount of these elements in the inner

scale layer to that in the base steel. In the case of silicon this ratio varies from 1.29 to 1.72, with chromium from 1.43 to 1.50, and with molybdenum from 1.29 to 1.70. It is interesting to note that in the case of chromium the degree of build-up is nearly constant even though the amount of this element in the base steel ranged from 0.07 to 5.09 per cent. With the remaining two elements the variation in the degree of concentration is more pronounced but again it is not excessive.

The results of these analyses presented in Table IV offer grounds for many interesting speculations, some of which will be discussed. For example, in the oxide layers it is observed that in every case the alloy content is lower in the outer portions than in the inner layer. This agrees with Pfiel's theory that the outer scale layers are composed of iron which had diffused through the base layer.

Table V

Degree of Concentration of Designated Alloying Elements in the Inner Scale Layer After 350 Hours at 1500 Degrees Fahr.

Type Steel	Ratio of Amount of Designated Element in Inner Scale Layer to that in Base Steel		
	Silicon	Chromium	Molybdenum
0.50 Mo	1.72	1.43	1.29
0.50 Mo + 1.35 Si	1.51	1.43	1.70
2 Cr + Mo	1.52	1.50	1.62
2 Cr + Mo + 1.32 Si	1.39	1.47	1.39
4-6 Cr + Mo	1.29	1.46	1.38
4-6 Cr + Mo + 1.55 Si	*	*	*

*Scale layer was of microscopic thickness and could not be analyzed.

Again all the elements in the steel surface except copper show a tendency towards lower values in the extreme outer steel layer, indicating that there may be some diffusion from the outer steel layer into the inner oxide layer.

The behavior of copper is an interesting field for speculation. This is the only element which is found in increased amounts in the outer steel layer, being present in one instance (2 per cent chromium plus 0.50 per cent molybdenum) in an amount representing a tenfold increase over the base metal. A clue to the mechanism of this effect is observed in the Si-Cr-Mo 5 steel which is the single steel type in this series that showed neither surface oxidation nor increased copper content on the surface. It would seem that the copper increment at the surface of the other steel types was deposited by that portion of the steel which was converted to oxide, and that some inward diffusion of the copper from the surface had occurred.

With one exception no copper was found in any oxide sample and in this case there is a possibility that the copper, a small amount of which was found in the inner scale layer, may have been carried into the sample mechanically from the steel surface.

Sufficient oxide was not found on the 4-6 Cr + Mo + 1.5 Si steel to permit analysis. In fact the surface of the specimen was barely tarnished. On the basis of the values given in Table V it would appear that the chromium content of the thin oxide layer on the surface of this steel would be of the order of 7.25 per cent, while the silicon content might range from 2.0 to 2.70 per cent. This would indicate that for an effective oxidation resistance at 1500 degrees Fahr. (815 degrees Cent.) a combined silicon plus chromium content of from 9.25 to 10.0 per cent is required in the inner scale. A chromium content alone of this magnitude would not be sufficient as is evident from the results presented for the 12 per cent chromium steel in Table III.

The microstructures of Figs. 5, 6 and 7 are included to show the surface of the specimens after 350 hours at 1500 degrees Fahr. (815 degrees Cent.). All of the scaled layer is not included as the magnitude of this can be readily seen from the photographs of Fig. 4. These structures definitely indicate that oxidation proceeded intergranularly although the extent of the intergranular attack was never far in advance of the general attack. At the magnification used this gave the appearance of surface pitting.

In the case of the 0.50 Mo and 2.0 Cr + 0.50 Mo type steels excessive grain growth occurred in certain sections under the given test conditions. With the low silicon 4-6 Cr + Mo steel, this test temperature was slightly above the thermal critical range and the grains remained small. Likewise the inner scale adhered more firmly to the surface of the steel than in the lower alloyed steels. With the higher silicon modification of this same steel, the test temperature was below the thermal critical range, the grain size remained small, and a thin layer similar to that obtained by decarburization was formed on the surface. It should be noted that no visible scale exists on the surface of this steel.

While the surface of the steel of Fig. 7b appears to be decarburized, there is likewise the possibility that this structure may have resulted from the diffusion of certain of the alloying elements of the steel into the thin layer of surface oxides. The subsequent elimination of grain boundaries might simulate decarburization.

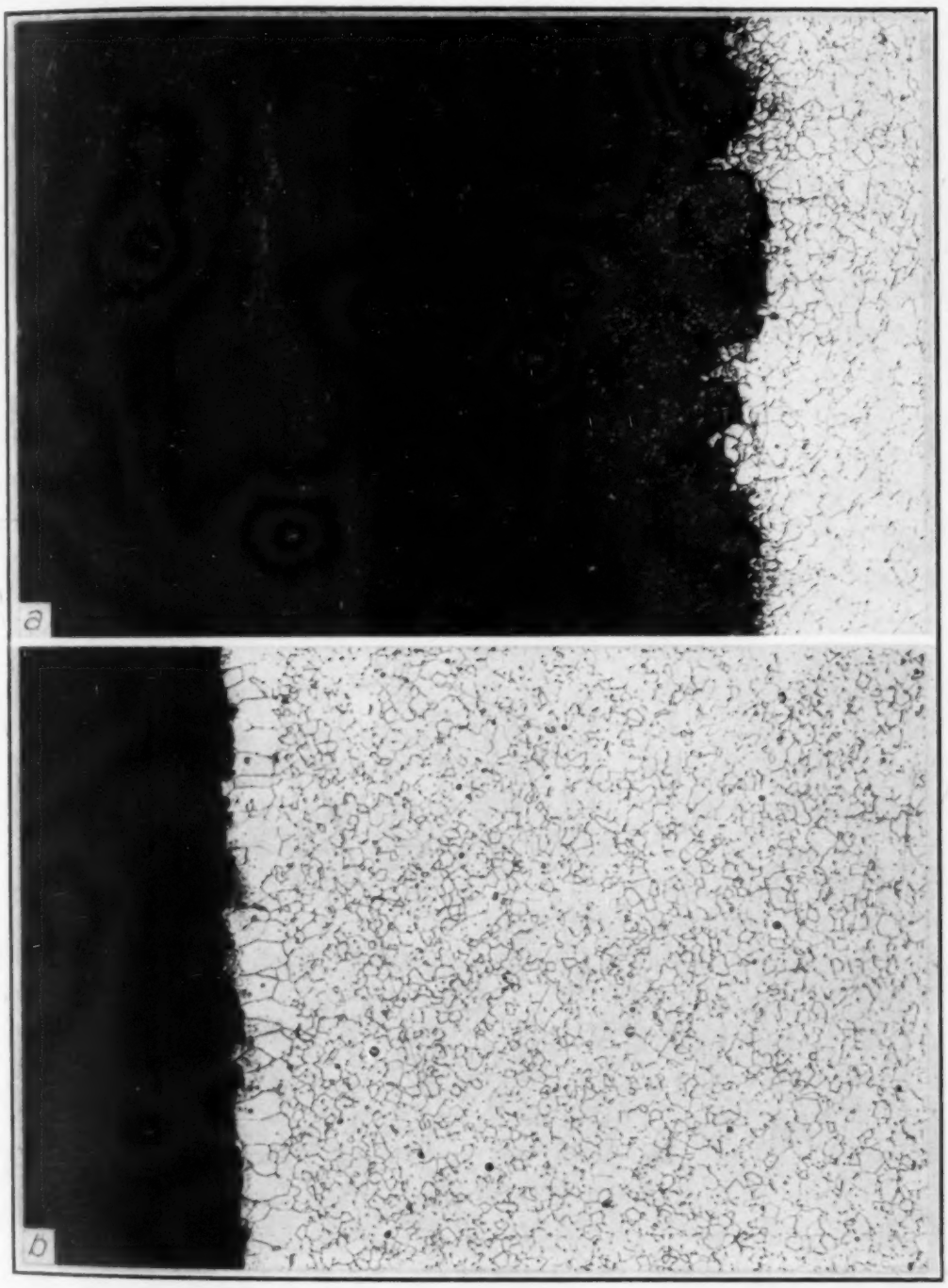


Fig. 7—Influence of Increased Silicon Content on the Surface of 4-6 Cr + Mo Steel After 350 Hours at 1500 Degrees Fahr.—× 100.
Fig. 7a—5.09 Cr, 0.55 Mo, 0.18 Si.
Fig. 7b—4.83 Cr, 0.51 Mo, 1.55 Si.

Summarizing it may be stated that the results obtained from both the chemical analysis and microscopic examination indicate that the increased oxidation resistance of certain alloy steels is due to the formation of a dense and tightly adhering scale which contains a

higher concentration of the alloying elements than are present in the base steel. This implies that diffusion of these alloying elements must occur and that, in order for a high resistance to be obtained, there must be a sufficient amount of these elements present to effectively combine with the oxygen which is diffusing inward. Likewise even in the absence of stress the attack proceeds intergranularly although the intergranular attack is never far in advance of the general attack.

Commercial Confirmation of Findings

Laboratory oxidation and corrosion tests are often considered as being of interest but not capable of direct commercial application. There is some basis for this belief as it is generally impossible to reproduce on a laboratory scale the exact service conditions, mainly because all of the variables are not known and because they may differ in each application. It is largely for this reason that corrosion tests were not considered in this investigation. However, in the case of the oxidation resistance, it is believed that laboratory tests should indicate, in a qualitative manner at least, the relative merit of the individual members of a series of steels.

It so happens that many of the steels considered in this investigation have been in service for a considerable period of time and a comparison of the service life with the laboratory records indicate the two to be in agreement. For example, tubes made of the Si-Cr-Mo 5 steel have been operating satisfactory at temperatures of 1300 to 1450 degrees Fahr. (705 to 790 degrees Cent.) for well over a year and the results of Table III show this steel to have a high degree of oxidation resistance at 1500 degrees Fahr. (815 degrees Cent.). Likewise increased life, due to lower scaling losses, has been obtained with the higher silicon modifications of the 0.50 per cent molybdenum steel at the intermediate temperatures.

Conclusions

The results obtained from the investigation on the influence of chromium, silicon and aluminum on the oxidation resistance of intermediate alloy steels permit the following conclusions:

1. A very high resistance to oxidation, at temperatures up to and including 1750 degrees Fahr. (955 degrees Cent.), can be obtained through the proper combination of these three elements.

2. In the presence of chromium, both silicon and aluminum appear to be more effective than chromium in improving the oxidation resistance. In fact for the steels considered silicon is seven times and aluminum four times as effective as chromium.

3. The addition of 1.5 per cent silicon to the 4-6 Cr + Mo type steel produces a high resistance to oxidation at temperatures up to and including 1500 degrees Fahr. (815 degrees Cent.), while the further addition of 0.50 per cent aluminum to this same steel greatly improves the resistance even at 1750 degrees Fahr. (955 degrees Cent.).

4. Chemical analysis showed a marked increase in the concentration of the chromium and silicon in the inner scale, thus supporting the theory that those elements diffuse, combine with the oxygen and form a dense and tightly adhering scale.

5. The microstructures indicate the attack to proceed intergranularly, even in the absence of stress, although it is not far in advance of the general attack.

6. Commercial service has confirmed the laboratory oxidation tests.

Acknowledgments

The authors wish to express their appreciation to officials of The Timken Roller Bearing Company for their financial support which made this investigation possible and for their permission to publish the findings.

DISCUSSION

Written Discussion: By P. A. E. Armstrong, consulting engineer, New York City.

The authors' paper contains a lot of very interesting information, but I must take issue with them concerning their statement on page 126:

> "These two elements (silicon and aluminum) have not been used to a wide extent for improving the oxidation resistance largely because of misconceptions with respect to their influence on the physical characteristics of the resulting steels."

There certainly has been and still is being used a large tonnage of chromium-silicon steels and chromium-silicon-aluminum steels that have been used because of their resistance to heat oxidation and their good physical properties.

The chromium-silicon steels under the name of Silcrome have been the subject of expensive litigation and adjudication of the patents, which patents were issued to me. Therefore I think I am right in saying that the chromium-silicon steels of this type have been very widely used and still are.

I would like to suggest to the authors that where aluminum is used with silicon, it should be higher than the silicon, and the scale resisting characteristics of aluminum-silicon steels with the very necessary chromium is better than a similar type steel without aluminum, and having the silicon content equal to the combined silicon and aluminum.

The very good scale resistance at 1750 degrees Fahr. the authors found in their steel 5-2-3 leads me to believe that the oxidizing conditions under the heat were not very severe. However, the marked effect of scale prevention of silicon over 2 per cent is clearly shown.

Molybdenum is a very useful addition as it increases the strength of the steel when hot, adds somewhat to its scale resisting characteristics and hardness and strength cold as clearly shown in Table II.

I would draw the authors' attention to many patents in this field which would tend to show the work that has been done and should modify the authors' opinion that they have not been used to any wide extent, and I am pleased to say that a number of these patents have been granted to me covering chromium-silicon steel, chromium-aluminum-silicon steel, and similar steel with nickel and other additions.

Written Discussion: By W. B. Mathews, Standard Oil Co., Chicago.

There is little that I can add to the very interesting treatment which the authors have given to this subject. However, it is perhaps worthy of note that the benefit of an aluminum addition in augmenting the oxidation resistance of these intermediate alloy steels appears to be confined to temperatures at which the low strength of such steels makes the use of any of them impractical. At temperatures in the usual range of application the aluminum-chromium-silicon steels appear to have little, if any, advantage over the silicon-chromium-molybdenum steels of comparable chromium content.

It is somewhat surprising that the intermittent tests on aluminum-chromium-silicon steels and silicon-chromium-molybdenum steels at 1250 and 1400 degrees Fahr. consistently showed lower losses than the continuous tests for, granting that the size and shape of the specimens were such that thermal stresses were at a minimum, it would appear that the losses in the intermittent tests would at least equal those in the continuous tests.

Written Discussion: By C. H. Fellows and R. M. VanDuzer, Jr., Detroit Edison Co., Detroit.

This subject of corrosion and oxidation resistance of steels is one of increasing interest to designers and users of equipment. The authors are to be commended for their contribution to the too meager supply of information now available.

The discussers have been interested in the corrosion of alloy steel from the standpoint of its attack by 1100 degrees Fahr. steam as part of an investigation conducted by The Detroit Edison Company in the use of high-temperature steam for power production since 1929. It so happens that two of the high-silicon steels listed in Table I of the paper were among those which were exposed to steam attack, together with two steels of practically the same composition but with only nominal silicon additions. These alloys are among those being investigated to determine their suitability for superheater tube use.

The specimens used consisted of unstressed ½-inch ground rods, 6 inches

long and exposed to periods of approximately 4000 and 8000 hours in 1100 degrees Fahr. steam. The compositions of these alloys were as follows:

	Chemical Composition, Per Cent by Weight						
Steel	C	Cr	Mo	Si	Mn	P	S
1	0.09	1.21	0.58	0.78	0.41	0.01	0.013
2	0.10	1.24	0.58	1.40	0.41	0.01	0.013
3	0.13	4.96	0.52	0.32	0.45	0.01	0.012
4	0.10	4.83	0.51	1.55	0.30	0.009	0.016

One set of these samples was removed after 4000 hours exposure and a second set was removed at the end of 8000 hours. Both of these groups were subjected to heating and cooling cycles; the 4000-hour set to 6, while the 8000-hour samples were exposed to 12. The result of weight-loss determinations is shown in the following tabulation:

	Weight Loss After Exposure to 1100 Degrees Fahr. Steam	
Steel	After 4000 Hr. (Grams per Sq. In. of Original Surface)	After 8000 Hr.
1	0.313	0.313
2	0.416	0.502
3	0.203	0.290
4	0.301	0.326

The comparative weight-loss values for high-silicon and low-silicon alloys as shown in this table are different from those obtained by the authors of the paper where the environment of the specimens was different from that of the specimens referred to in the table above. Such data prompt the observation that general conclusions regarding the scaling resistance of steels cannot be drawn from data resulting from any one type of reactive environment. In comparing actual samples from steam corrosion tests with those of the authors' from electric muffle furnace tests, a distinct difference is noted in the physical character of the scale. That on the furnace samples tends to be loose and flaky, whereas that on the steam specimens is dense and tenacious.

If oxidation and corrosion results are to be of maximum use to designers of high temperature equipment, rate of loss should be given rather than the weight loss for any one period as has been done by the authors. The steam corrosion work conducted by the discussers would indicate that the maximum rate of scaling takes place during the first few thousand hours of exposure in all except carbon steel. There is no reason to believe that the shape of the rate loss curve for air oxidation would be materially different than for steam corrosion, although the total amount of scale formed in the two reactive mediums might be materially different.

To the writers' knowledge there is no information available in the literature as to the effect of stress on the rate of scale formation. The tests reported in this paper as well as the steam corrosion work mentioned have been conducted on unstressed specimens. The discussers are inclined to believe that, at temperature of 1100 degrees Fahr. and above, the inner scale layer is ductile enough to insure considerable protection against scaling if the stress and resultant creep are not excessive. The authors' comments on this matter would be of interest.

Authors' Reply

We appreciate the discussion which has been offered to this paper as it will guide our future work on this subject.

With respect to the discussion of Messrs. Fellows and VanDuzer, the results presented are of great interest as they shed further light on the general subject of surface stability. It should be realized, however, that the present paper is concerned with oxidation resistance, such as would be encountered commercially in either air or flue gases, while the discussion pertains to corrosion in steam. A comparison of the results from the two types of test definitely indicates the mechanism of attack to be different. Realizing this, work is now in progress attempting to establish the mechanism in the presence of steam.

As stated in the paper the results presented are intended to be qualitative, rather than quantitative, and for this purpose the total oxidation loss over the 1000-hour testing period was believed to be the most suitable index for presentation. The study of oxidation rates is complicated by the primary and secondary rates, each of which may be influenced to a pronounced degree by various factors, and to different degrees as the compositions of the steel or the attacking media are varied.

Insofar as the influence of stress is concerned, it is believed that the presence of stress may cause intergranular attack, in certain types of steels, to be far in advance of the general attack. In the absence of stress, the attack is largely general in nature.

One statement of this discussion may be misinterpreted. It is stated that the scale produced in the air oxidation tests tended to be loose and flaky. What was really meant was that it was somewhat more easily removed than that produced in the steam corrosion tests. Both scales were, however, dense and tenacious.

With respect to Mr. Mathews' comments, the increased oxidation resistance at 1750 degrees Fahr. imparted by the aluminum additions is recorded as a matter of interest. The primary purpose of the aluminum additions was, however, to decrease the air hardening characteristics and to improve the corrosion resistance, especially to hot petroleum products. The greater oxidation resistance obtained at 1250 and 1400 degrees Fahr. from the intermittent tests is believed to be due to the more rapid formation of a protective scale layer on the surface.

We agree with Mr. Armstrong that steels containing silicon and aluminum have been used commercially for obtaining increased resistance to oxidation. Our statement with respect to the limited use of these two elements was intended to apply mainly to seamless tube applications.

INFLUENCE OF ALUMINUM ON CAST CORROSION RESISTING STEEL

By Joseph A. Duma

Abstract

The paper describes some of the alloying effects of 0.08 to 3.00 per cent aluminum on the mechanical and corrosion properties of cast 20-10 corrosion resisting steel. The effect on mechanical properties was studied with tensile, bend, hardness, and impact tests. Corrodibility was tested in four of the common corroding media, namely: boiling 67 per cent nitric acid, 4 per cent sea salt spray, tide river water, and 10 per cent ferric chloride solution. An oxidation test was also performed. Photographic evidence regarding the effects of aluminum on both the macro- and microstructures of this metal is presented. Studies of the response to heat treatment of aluminum-bearing corrosion resisting steel are likewise included.

IN THE manufacture of Grade 1 corrosion resisting steel castings for the Navy, it is the practice of the Navy Yard to finish off each heat with an addition of 0.15-0.30 per cent titanium. The reasons for, and the mode of, that addition have been given in a recent A.S.M. paper by the author.[1] In this process the metal is melted down—first, under a cover of molten lime-alumina slag, and second, under a highly reducing lime-aluminum slag. Immediately prior to pouring, the titanium is introduced into the bath in the form of a mixture consisting of 2 parts titanium oxide (rutile) and 1 part aluminum shot. The two materials react exothermically and are thereby converted into two new materials, titanium and molten aluminum oxide slag. The use of aluminum in both the slag and the rutile mixture not infrequently results in the incorporation of some residual aluminum in the metal, generally ranging in content from 0.06 to 0.12 per cent. Hitherto, the extent to which this residual aluminum benefited or injured the corrosion and mechanical proper-

[1]Joseph A. Duma, "Effect of Titanium on Some Cast Ferrous and Nonferrous Metals," Transactions, American Society for Metals, Vol. XXV, No. 3, Sept. 1937.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The author, Joseph A. Duma, is assistant metallurgist, Norfolk Navy Yard, Portsmouth, Virginia. Manuscript received June 18, 1938.

ties of the metal was a matter of conjecture. In order to achieve better control over the manufacture of corrosion resisting steel with the thermit process of titanium addition it was deemed desirable to evaluate these effects. Being slight, and therefore difficult of isolation, they were accentuated with deliberate additions of aluminum. The additions, as will be shown later, were made both in the furnace and in the ladle, with and without rutile.

Melting Practice

The heats for this investigation were all made in a basic-lined, one-half ton, Moore "Lectromelt" arc (three 3-inch electrodes) furnace. The initial charge for each of these heats was as follows:

(1) 1000 pounds corrosion resisting steel plate scrap ($\frac{3}{16}$ x 8 x 12 inches).
(2) 500 pounds foundry returns (heavy corrosion resisting steel gates and risers).
(3) 30 pounds black nickel oxide (77 per cent nickel).
(4) 15 pounds red hematite ore (½-2-inch lumps).
(5) 50 pounds fluorspar (92 per cent CaF).
(6) 50 pounds low silica lime (97 per cent CaO; 0.50 per cent SiO_2).

Approximately 100 pounds of item (1) were charged first, then items (2) to (6) inclusive, and finally the remainder of item (1). The carbon electrodes, precleaned with air blasting as a precaution against carbon pick-up, were lowered onto the charge and the power of the high tap (145-volt arc) was turned on. The entire charge was melted down in approximately 20 minutes. The resulting lime slag was thinned down with 10-12 pounds alumina. This thin, grey slag was kept on the metal from 5 to 10 minutes; it was then cleaned off and replaced with one consisting, when first made, of 10-12 shovelfuls of low silica lime. From time to time, in the course of refining, the newly made slag was occasionally sprinkled with half shovelfuls of a 1:3 Al_2O_3-CaO mixture. During the interval between slagging off and final pouring the furnace was supplied with power from the low, and next to the low, taps (80 and 100 volt arcs). At the halfway mark of the refining stage approximately 50 pounds of 70 per cent ferrochromium, together with about 1 to 2 pounds of 95 per cent ferrosilicon, were incorporated into the bath. This addition was not made at one time but split in two, and introduced into the bath five minutes apart. At the end of the final chromium addition the furnace was tilted, and some of the second slag (colored green)

was run off. The final slag was repaired with several shovelfuls of Al_2O_3-CaO. The bath was then ready for the final alloy addition, i.e., titanium, which, as previously stated, was added to the bath in the form of a mixture made up of 36 pounds rutile and 18 pounds aluminum shot. An intense exothermic reaction immediately occurred between the rutile (titanium dioxide) and the aluminum, resulting in their simultaneous reduction and oxidation. At the completion of the thermit reaction the metal was poured into a 1-ton, bottom-pour ladle and thence into "dry" steel sand molds. The final slag was white on the top, dark to black in the center, and pink underneath.

Particular attention is directed to the fact that neither limestone nor pulverized coke was used at any time in the manufacture of these metals. The high recovery of manganese and silicon should also be noted: this, of course, signifying a comparatively low degree of oxidation even in the melt-down.

With the exception of Heats 9, 10, 11, and 12, which were made of only 1000-pound burden instead of the usual 1500-pound, all the heats listed in Table I were made as outlined above. The rutile-aluminum and aluminum additions varied with each individual heat as follows:

Heat No.	Titanium Additions: Rutile plus Aluminum (95%-98% TiO_2) Lbs.	(Shot; 99% Al) Lbs.	Aluminum Additions (Pig; 99.9% Al) Lbs.	Per Cent of Each in the metal: Ti	Al
1	36	18	None	0.24	0.12
2	30	15	None	0.24	0.08
3	30	15	5[1]	0.21	0.24
4	32	16	None	0.29	0.07
5	32	16	10[1]	0.28	0.48
6	32	16	10	0.27	0.20
7	30	15	15	0.42	0.40
8	24	12	38	0.17	1.10
9[2]	25	25[3]	20	0.80	1.24
10[2]	None	None	26	...	1.76
11[2]	20	10	45	0.52	3.25
12[2]	80	45	None	3.10	0.62

[1] Added to ladle.
[2] 1000-pound heats.
[3] Grained aluminum-rutile, 1:1 mixture (TiO_2 = 75 per cent).

The pouring temperature range was approximately from 2775 to 2875 degrees Fahr. (1525 to 1600 degrees Cent.). The melter estimated the temperature by the spoon test before tapping the heat but the actual temperature was taken with an optical pyrometer as the metal poured over the spout of the furnace. Steel from each heat was poured into two test blocks, each block weighing approximately

350 pounds. The main body of the block consisted of a slab 30x9x2 inches, with twelve coupons 9x1½x2 inches cast on the bottom side. Test blocks were made in dried sand molds; coupons were removed from the block by melting with the metallic arc.

Table I
Composition of Corrosion Resisting Steels

Heat No.	Chemical Composition, Per Cent								
	C	Mn	P	S	Si	Ni	Cr	Ti	Al
1	0.12	0.58	0.010	0.012	0.40	10.60	22.63	0.24	0.12
2	0.14	0.45	0.037	0.010	0.67	10.75	21.75	0.24	0.08
3	0.14	0.45	0.037	0.010	0.67	10.75	21.75	0.21	0.24
4	0.10	0.50	0.030	0.003	0.63	10.66	22.41	0.29	0.07
5	0.10	0.50	0.030	0.003	0.63	10.66	22.41	0.28	0.48
6	0.23	0.47	0.030	0.010	0.45	10.93	21.14	0.27	0.20
7	0.10	0.54	0.013	0.008	0.72	10.58	21.33	0.42	0.40
8	0.11	0.86	0.030	0.010	1.17	10.60	20.53	0.17	1.10
9	0.11	0.55	0.030	0.010	1.14	10.78	20.71	0.80	1.24
10	0.12	0.55	0.010	0.012	0.80	10.95	21.90	...	1.76
11	0.13	0.52	0.020	0.006	1.15	13.65	20.63	0.52	3.25
12	0.13	0.64	0.025	0.007	0.66	11.57	22.47	3.10	0.62

Tests and Test Specimens

(a) *Chemical Analyses*—Chemical analyses were made using standard recognized procedure for the accurate determination of all elements. The titanium determinations were made according to the colorimetric method of Cunningham;[2] the per cent aluminum was found using the mercury cathode method of separation.[3]

(b) *Tensile Tests*—All tensile specimens were of the standard cylindrical type, with a 2-inch gage length and 0.505-inch diameter and the specimens were pulled in an Amsler hydraulic testing machine of 50,000 pounds capacity.

The proof stress was taken as that load which when released produced a permanent set of 0.0002 inch in a 2-inch gage length.

The yield point could not be detected by the usual drop of beam method on these austenitic and ferritic-austenitic alloys. It was found with a pair of dividers and was taken as the stress at which the divider point first failed to re-enter the 2-inch gage mark.

The results listed in the tables are the average values obtained from testing duplicate specimens but when there was a large discrepancy in results of these duplicate specimens a third specimen was

[2]T. J. Cunningham, "Determination of Titanium in Plain Carbon and 18-8 Nickel-Chromium Steels," *Industrial and Engineering Chemistry*, Vol. 5, No. 5, p. 305-6, Sept. 15, 1933. Analytical Edition.

[3]Hillebrand and Lundell, "Applied Inorganic Analysis," p. 105, published by John Wiley & Sons Incorporated.

subjected to the same treatment and the average taken from the two giving most similar values.

(c) *Hardness Tests*—The Brinell hardness readings were taken on the grip ends of broken tensile specimens which had been machined flat on opposite sides in a milling machine. In all Brinell tests a 3000-kilogram load, a 10-millimeter ball, and a 30-second application of load were used.

(d) *Impact Tests*—Izod impact specimens were the standard 10-millimeter square bars, notched transversely on two adjacent sides

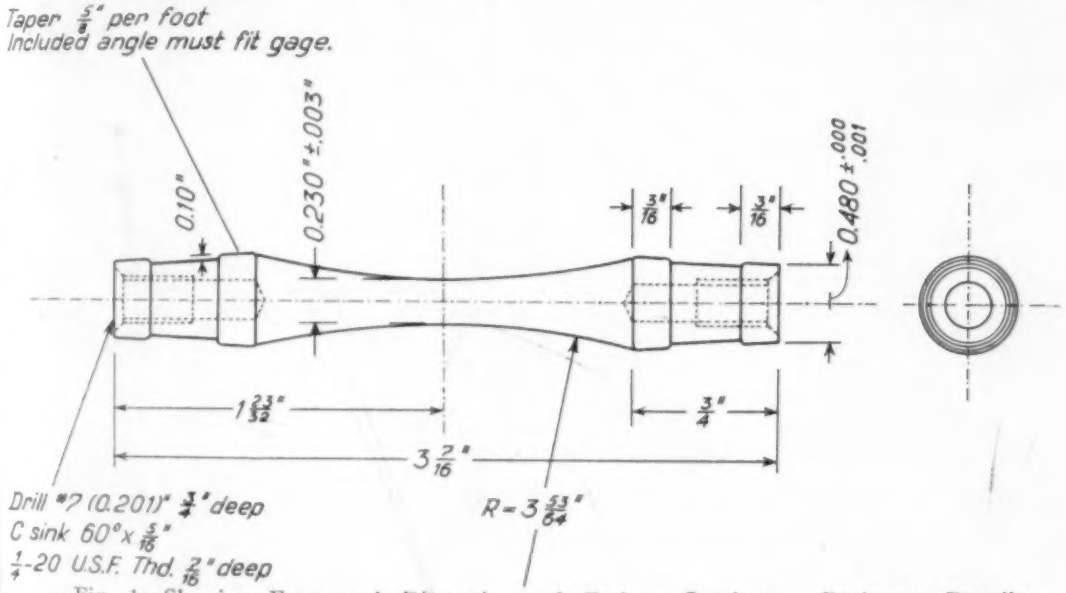


Fig. 1—Showing Form and Dimensions of Fatigue Specimen. Designer: Battelle Memorial Institute.

by a "V" cutter to a depth of 2 millimeters and an angle of 45 degrees. The notch was finish machined with a second cutter that was frequently ground and honed with a radius of 0.01 inch on the points. Impact tests were made in an Amsler pendulum impact testing machine of 240 foot-pounds capacity, equipped with an Izod head and anvil. The pendulum was let fall from the 120 foot-pound graduation on the Izod scale.

(e) *Fatigue Tests*—Fatigue specimens were machined to the form and dimensions shown in Fig. 1. The values for endurance limit were determined on a Moore rotating beam type fatigue testing machine operating at 1800 revolutions per minute.

(f) *Micro-Specimens*—Specimens for microscopic examination were taken from the large ends of broken tensile bars. Macro-specimens were made from coupons similar to those used for the tensile test.

(g) *Corrosion Tests*—Five different corrosion tests were applied to the steels studied in the investigation. A description of each follows:

(1) Salt-spray: The specimens used in the salt-spray corrosion tests were of the plumb-bob type and finished with dry No. 00 iron-free emery cloth. Prior to testing, all specimens were washed in the following cleaning agents, in this order: petrolic ether, alcohol, warm water, alcohol.

The salt-spray test was conducted by exposing the specimens to a finely divided spray generated by a hard rubber atomizer using air at 15 pounds pressure and a 4 per cent sea-salt solution. The chemical composition and alkalinity of the salt used were:

Sodium chloride (NaCl), per cent	98.78
Insoluble in water, per cent	1.01
Lime (CaO), per cent	0.10
Magnesia (MgO)	Trace
Oxide of iron (Fe_2O_3)	None
Moisture or loss at 221 degrees Fahr. (105 degrees Cent.), per cent	0.10
pH value of a 4 per cent solution in tap water	7.4–7.5
pH value of a 4 per cent solution in distilled water	7.4

To attain maximum uniformity of exposure, every specimen was periodically rotated 180 degrees so as to face the fog and all specimens were alternately transposed from one rack to the other. The average prevailing test temperature was 77 degrees Fahr. (25 degrees Cent.), and the total time of exposure was 1000 hours.

(2) Wet and dry box: Solid cylinders, 1 inch in diameter by 2½ inches high and topped with a 45-degree cone one inch high, were used for specimens in this test. They were given the standard, dry No. 00 iron-free emery cloth finish.

The specimens were exposed to alternate wet and dry conditions in an outdoor tank which was automatically filled with, and emptied of, tide river water at definite intervals (3 times an hour). Having been in the box for 11 months, the number of cycles of wetting and drying to which the specimens were exposed was slightly in excess of 24,000. The salinity of the southern branch of Elizabeth River, whose water was used in the test, is subject to seasonal variation. A representative analysis of this water follows:

Total Solids	43.7 grams per liter
Sodium Chloride	34.6 grams per liter
Sodium Sulphate	3.5 grams per liter
Magnesium Chloride	5.6 grams per liter
Specific Gravity (60 degrees Fahr.)	1.0135

(3) Oxidation Test: Finished ground, rectangular disks, ½x 2¼x2¼ inches, were heated to 1950 degrees Fahr. (1060 degrees Cent.) and held at temperature for 1 hour. They were then air-cooled to room temperature and pickled in 50 per cent hydrochloric acid (specific gravity 1.19) solution maintained at 170 degrees Fahr. (76 degrees Cent.) until all the scale was removed. The above procedure was repeated five times.

(4) Nitric Acid: The specimens for nitric acid test were 2x½x ¼ inches.

The test was conducted by immersing each specimen in 400 milliliters of chemically pure 67 per cent concentrated nitric acid (specific gravity 1.42) contained in flasks equipped with reflux condensers. Dilution of the 67 per cent acid solution was accomplished by using distilled water. The flasks were heated until boiling occurred and were maintained at boiling temperature for forty-eight hours after which the samples were withdrawn, washed, dried, and weighed. The foregoing procedure was repeated three times on each specimen.

The corrosion losses are expressed in inches penetration per month and were calculated after each 48-hour period from the formula:

$$R = \frac{43.9\,W}{A\,S\,T}$$

where

R = Corrosion rate in inches penetration per month.
W = Weight loss in grams.
A = Total area in square inches.
S = Density in grams per milliliter.
T = Time in hours (48).

(5) Ferric chloride pitting test: To reduce edge attack to a minimum, the specimens were made spherical in form with a diameter of 1 inch. Surface markings were removed by polishing on metallographic papers No. 00, 000, 0000, and finally velvet and levigated alumina; cold work effects in the surface skin were reduced to a very low value with repeated and alternate polishing and etching of each specimen.

The specimens were placed in a 10 per cent ferric chloride solution contained in beakers (capacity: 200 cubic centimeters). The solution was prepared by dissolving 100 grams of $FeCl_3 \cdot 6H_2O$ in

approximately 500 cubic centimeters of distilled water containing 20 cubic centimeters of 2.45 normal hydrochloric acid at 150 to 170 degrees Fahr. (65 to 70 degrees Cent.). After five minutes the above solution was diluted with distilled water to 1 liter. The pH of the final solution was 1.1.

Influence of Aluminum on Corrosion Resisting Steel

Castability: The influences of aluminum on molten corrosion resisting steel are several. Perhaps the most important feature is its influence on fluidity. As in brass founding[4] and galvanizing,[5] so in the manufacture of austenitic chromium-nickel alloys, aluminum, through its action on surface tension, renders metal more fluid. The running quality of aluminized corrosion resisting steel manifests itself in its searching action, filling completely the thinnest spaces (drag and cope interfaces), and in its tendency to form fins and flat thin sheets when spilled. The influence of aluminum on the surface appearance of castings also merits recording. Aluminum bearing castings, in contradistinction to the straight corrosion resisting steel castings, are generally smoother when cast in sand molds of identical physical properties. Apparently, aluminum-treated metal is not as damaging in its effects on mold sand as straight corrosion resisting steel.

Physical Properties: Fig. 2 is a graph of the physical properties of Heats 1, 5, 8, and 10 after water quenching from 2000 degrees Fahr. (1095 degrees Cent.). Each of these heats, it will be noted, aside from being low in titanium, is similar in composition. An examination of Fig. 2, together with a study of the physical data contained in Table II, shows:

(1) That the presence of aluminum in amounts from 0.07 to 1.50 per cent has a materially strengthening effect upon corrosion resisting steel, since it raises the tensile strength and yield point without unduly affecting ductility or impairing shock resisting quality.

(2) That additions of aluminum from 1.75 to 3.25 per cent effect substantial increases in tensile strength, yield point, and hardness, but at the sacrifice of considerable ductility.

(3) That the incorporation of more than 2.00 per cent aluminum as a component of the composition of corrosion resisting steel

[4]Vickers, "Metals and Their Alloys," p. 415, published by Henry Carey Baird & Co., Inc., New York City.

[5]U. S. Dept. of Commerce, Bureau of Standards Circular No. 395, "Zinc and Its Alloys," p. 118.

castings is of doubtful benefit, for it embrittles them to a degree so damaging as to render them unfit for applications demanding high resistance to suddenly applied impact loads.

In short, titanium-bearing corrosion resisting steel of the type studied in this investigation can be made to have a comparatively high combination of tensile strength and ductility if the aluminum content is restricted to approximately 1.50 per cent.

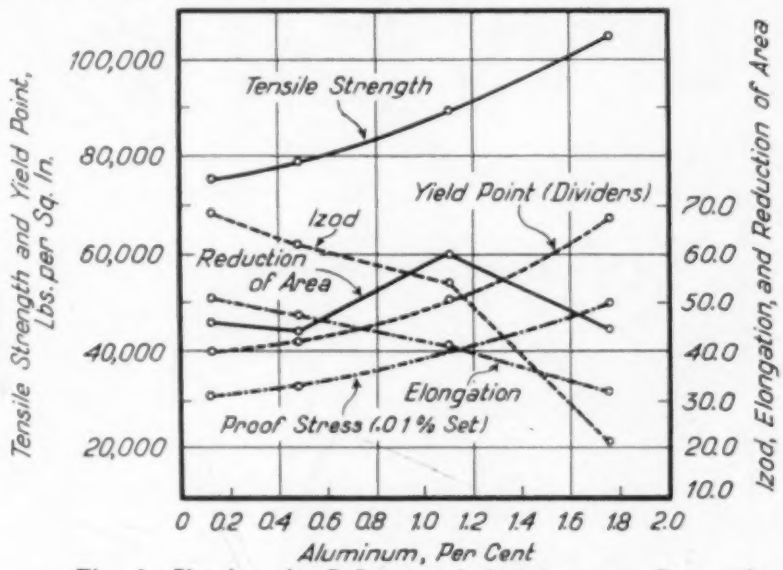


Fig. 2—Showing the Influence of Aluminum on Cast and Annealed—Quenched in Water from 2000 Degrees Fahr. (1093 Degrees Cent.)—20-10 Corrosion Resisting Steel.

Tests to determine the influence of aluminum on the fatigue strength of cast 20-10 containing titanium were also made, but due to the limited number of specimens tested, it was impossible to obtain a complete endurance curve. Within the scope of the investigation, it appears that an increase in fatigue life can be expected with increasingly higher amounts of aluminum and titanium in combination where these elements cause an increase in tensile strength. The increase in fatigue strength, however, is not in the same order as increase in tensile strength. Table II shows that the endurance limit of aluminum-titanium corrosion resisting steel is approximately 35 to 40 per cent of its tensile strength.

Physical Properties After Forging: Several cast coupons from Heats 1, 9, and 10—rough machined all over for removal of as-cast surface to 2x2x6 inches—were preheated slowly to 1600 degrees Fahr. (870 degrees Cent.), soaked, and then heated rapidly to 2350 degrees Fahr. (1290 degrees Cent.). The specimens were reduced by forging with light but rapid strokes to bars ⅝ inch in diameter. At

Table II

Physical Properties of Al- and Ti- Containing 20-10 Corrosion Resisting Cast Steels(a)

Heat and Specimen Number	Ultimate Tensile Strength psi	Tensile Properties				Impact	Fatigue Properties			
		Yield(1) Point psi	Proof(2) Stress psi	Elongation Per Cent	Red. of Area Per Cent	Cold(3) Bend Deg.	Izod Ft.-Lbs.	Maximum Fiber Stress psi	Cycles To Failure	Endurance Limit psi	Ratio Per Cent Fat. Str. U.T.S.
1	76,250	40,000	31,000	51.0	46.32	180	69				
2	75,500	39,750	.....	52.0	62.24	180	..				
3	75,750	40,000	.....	50.5	63.28	180	..				
4	77,250	41,500	.....	51.0	44.56	180	62	30,000	102,410,000*	30,000+	38.8
Retested at								40,000	33,400,000*		
5	78,000	42,250	32,750	48.0	44.27	180	62				
6	77,750	41,000	.....	47.0	41.58	180	..				
7	81,250	42,750	.....	49.0	60.56	180	83	30,000	102,412,100*	30,000+	36.9
Retested at								40,000	5,430,400		
8	89,500	51,250	42,000	42.5	60.35	180	54				
9-A	108,500	71,000	52,500	20.0	30.50	90	12	53,000	3,900		
9-B								30,000	123,128,500*	30-40,000	27.6-36.8
Retested at								35,000	105,052,100*		
Retested at								40,000	76,906,200*		
Retested at								45,000	51,756,400*		
Retested at								50,000	28,850,900		
9-C								40,000	4,367,900		
9-D								35,000	538,200		
10	105,000	67,750	50,250	32.5	44.86	120	21				
11	124,000	82,750	62,500	4.5	7.0	10	8	45,000	32,056,000	45,000—	36.3
12	122,250	84,000	.....	3.0	3.5	2	0				

(a) All specimens annealed by quenching in water from 2000 degrees Fahr.
(1) Divider Method.
(2) 0.0002-inch permanent deformation in 2 inches.
(3) Bent around a 1½-inch pin.
*No failure—test terminated.

no time during forging was the temperature of the work permitted to drop below 1800 degrees Fahr. (980 degrees Cent.). The forged bars, after annealing (quenching in water from 2000 degrees Fahr.), gave the following physical values.

Heat	Tensile Strength Lbs./Sq. In.	Yield Point* Lbs./Sq. In.	Elongation Per Cent	Reduction of Area Per Cent
1	94,750	44,500	51.5	52.5
9	107,000	85,750	29.5	49.5
10	105,000	75,000	35.0	50.5

*Dividers.

Forging augments noticeably the tensile strength of corrosion resisting steel containing incidental (under 0.12 per cent) aluminum.

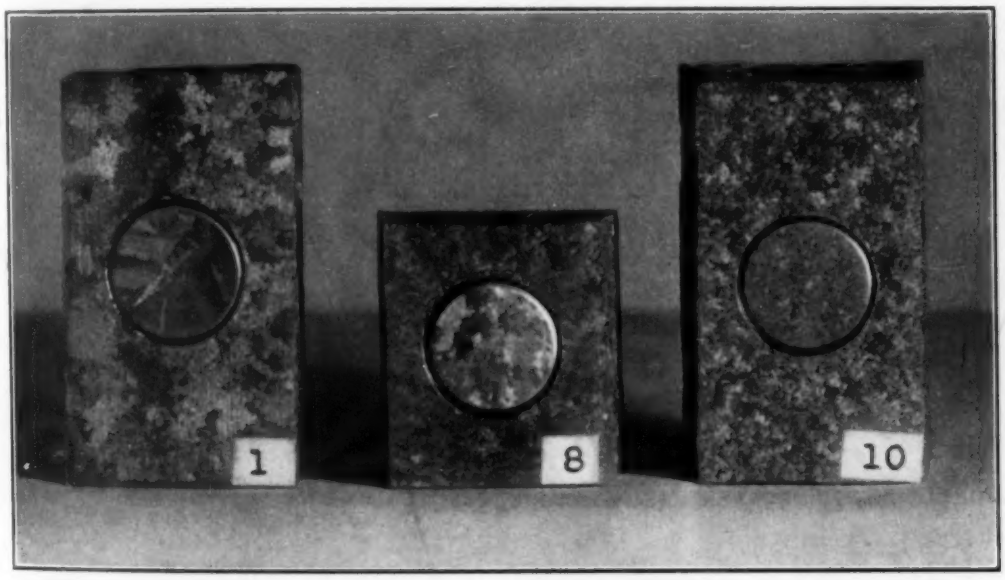


Fig. 3—Macro-etched CRS, Showing the Influence of Aluminum on Primary Crystallization. Natural Size.

The yield point and not the tensile strength is augmented in corrosion resisting steel containing larger amounts of (1.24 and 1.76 per cent) aluminum.

Structure (Macro and Micro): Increasing amounts of aluminum exert a refining influence on the grain structure of castings. The grain refining propensity of aluminum is most strikingly evidenced in the decrease of surface roughening over the gage length of pulled tensile specimens. Macrostructurally, the positive action of aluminum in producing a very small grain size is set forth in Fig. 3. It will be noted that specimen 1, made from low aluminum Heat 1, is fairly coarse-grained while specimens 8 and 10, containing

1.10 and 1.76 per cent aluminum respectively, are fine-grained. The large specimens were macro-etched in hot 38:12:50 HCl-H_2SO_4-H_2O etching solution for 10 minutes; the micro buttons—fitted into the face of the large specimens—were etched separately in Vilella's (mixed acids in glycerol) micro etching solution. The micro buttons were taken from the grip end of tensile bars made from the same coupons as the macro specimens.

The effect of aluminum on the microstructure is depicted in Figs. 4 to 9 inclusive. The most apparent, if not the most noteworthy, structural change induced by aluminum in solid solution is a partial suppression of the formation of austenite, or conversely, the promotion of insular ferrite. The structure of Heat 1, which contains 0.12 per cent aluminum, is one consisting of a comparatively few alpha-delta pools embedded in a matrix of austenite, while that of Heat 10, analyzing 1.76 per cent aluminum, is constituted of nearly equal amounts of the gamma and alpha-delta phases. The high aluminum structures etched rapidly, and with pronounced darkening of the ferrite.

The effect of aluminum on the gamma iron loop is thus one which tends to compress or pull it in from the left to the right. Other elements affecting ferrite formation in a manner analogous to aluminum are chromium, silicon, titanium, molybdenum, vanadium, and tungsten; those suppressing ferrite formation are carbon and nickel.[6] Much of the effect of aluminum on the mechanical properties and corrosion resistance of the subject steels is due to both its ferrite-forming and grain-refining tendencies.

Heat Treatment: In order to determine the effect of aluminum upon the response of corrosion resisting steel to various annealing treatments, and to discover whether it produces age-hardening, as it does in K-Monel, a number of exploratory heat treatments were given to Heat 9. Along with each specimen from Heat 9 a comparison specimen from Heat 1 was used. The size of all specimens was alike, i.e., 1½x1½x2 inches.

The effects of the variables, holding time and annealing temperature, were studied first. Figs. 10 and 11 are illustrative of the influence of the foregoing variables on the Brinell hardness of Heats 1 and 9. Briefly, hardness increases with holding time and temperature, the highest values being obtainable after a sojourn of 1 to 1½

[6]The Book of Stainless Steels, published by the American Society for Steel Treating, Cleveland, Ohio, Chapter 14, p. 347.



Fig. 4
Fig. 5
Fig. 6
Fig. 7

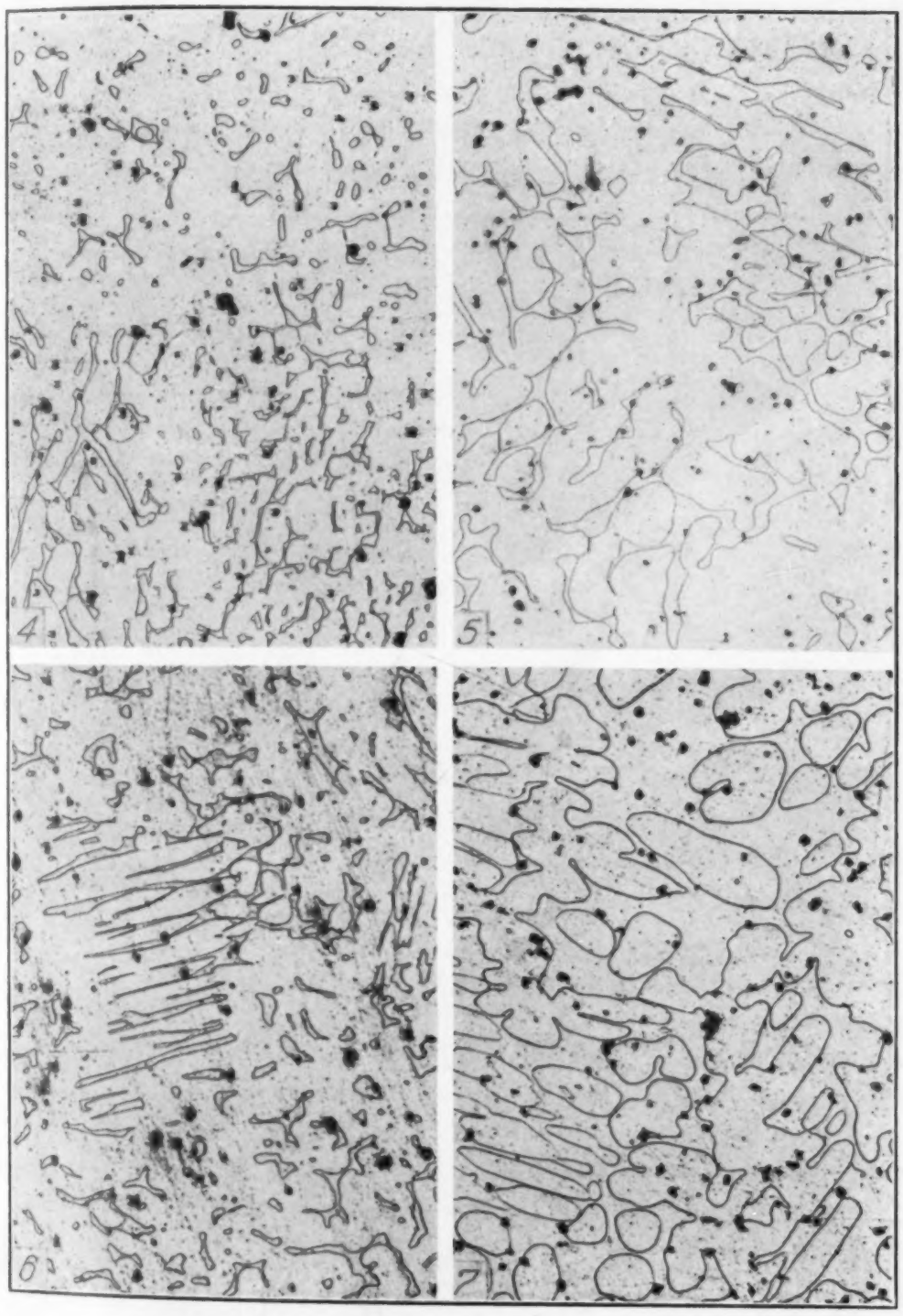


Fig. 4—Heat No. 1, Etched. Alpha-delta Pools in an Austenitic Matrix, × 100.
Fig. 5—Heat No. 7, Etched. Alpha-delta Pools in an Austenitic Matrix, × 100.
Fig. 6—Heat No. 8, Etched. Alpha-delta Pools in an Austenitic Matrix, × 100.
Fig. 7—Heat No. 9, Etched. Alpha-delta Pools in an Austenitic Matrix, × 100.

hours at 2150 to 2200 degrees Fahr. (1178 to 1202 degrees Cent.).

Age-hardening was studied on two differently treated sets of specimens. The specimens of one set were quenched in water from 2300 degrees Fahr. (1260 degrees Cent.) after an hour's exposure to the high temperature; those of the other set were quenched simi-

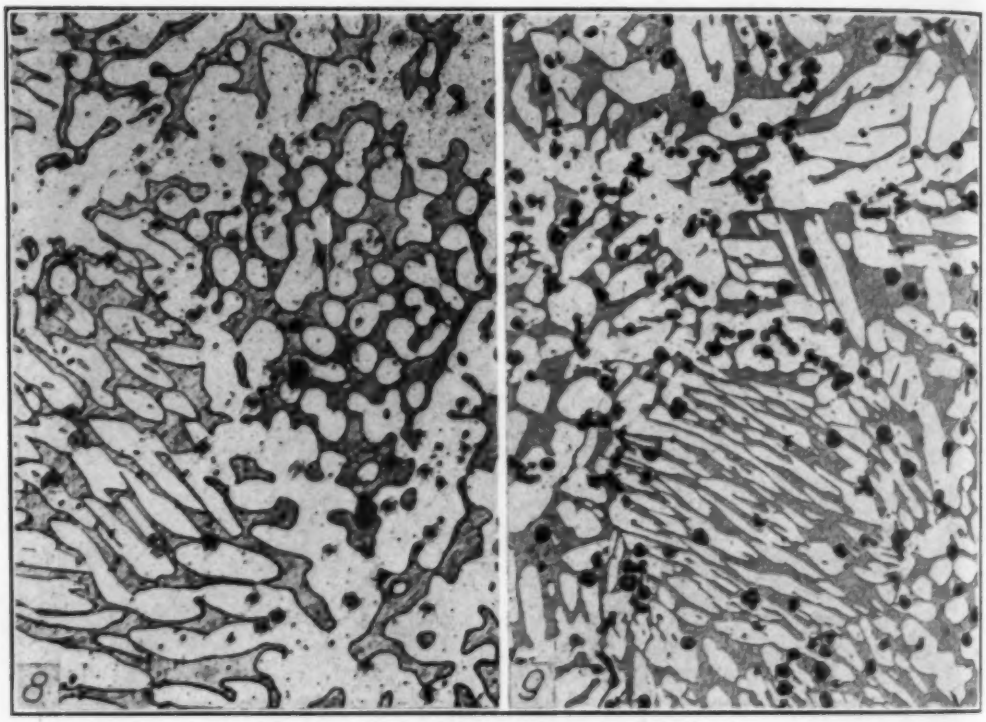


Fig. 8—Heat No. 10, Etched. Alpha-delta Pools in an Austenitic Matrix, × 100.
Fig. 9—Heat No. 11, Etched. Gamma Iron Pools in a Matrix of Alpha-delta Ferrite.

larly but from 2000 degrees Fahr. (1095 degrees Cent.). Two specimens from each set were then tempered for 8 hours at various aging temperatures ranging from 750 to 1450 degrees Fahr. (390 to 790 degrees Cent.). The hardness curves in Fig. 12 show a prominent peak at 950 degrees Fahr. (510 degrees Cent.), indicating definitely that precipitation hardening has taken place.

Some of the unusual results of the exploratory heat treatments were checked on large specimens from which standard tensile bars were made. The heat treatments given these specimens, together with the physical properties obtained, are shown in Table III.

Corrosion Resistance

Salt-spray: The specimens shown in Fig. 13 were exposed to a 4 per cent sea salt fog for 1000 hours. Similar specimens, made

from Heats 3, 5, 6, 7, and 8, were also tested along with those shown in the photograph. An examination of the specimens in Fig. 13 disclosed that, from left to right, the third, sixth, and eighth (Heats 1, 10, and 11) plumb-bobs had a rating equal to "A," representing an ideal condition and being practically perfect as regards resistance to

Table III
Physical Properties After Various Heat Treatments

Heat No.	Heat Treatment: Annealing Temp. °F.	Annealing Hold Hrs.	Annealing Coolant	Aging Temp.	Aging Hold	Aging Cool	Tensile Properties: T. S. psi	Y. P.* psi	Elong. %	R.A. %	Brinell Numeral
10	(As-cast)		.....				84,250	35,000	30.0	36.22	...
10	2100	1	Water	...	.	....	105,500	68,000	32.5	44.86	...
10	2050	1	Water	975	8	Fur.	109,250	71,250	12.5	11.90	...
9	(As-cast)		.....				84,250	40,000	32.5	40.97	166
9	2100	1	Water	...	.	....	107,750	69,000	20.0	30.50	223
9	2100	1	Water	950	8	Fur.	107,250	71,000	7.5	8.53	232
9	2150	1	Water	950	8	Fur.	108,500	69,000	9.0	9.66	238
11	(As-cast)		.....				98,250	77,500	3.5	4.77	...
11	1650	2	Furnace	...	.	....	80,700	.....	1.0	2.35	...
11	1800	1	Water	...	.	....	117,000	80,000	4.0	5.86	255
11	2300	1	Water	...	.	....	Cracked in lathe while machining.				

*Dividers

corrosion under the prescribed test; the others showed some attack on the metal but practically no progressive corrosion. From a study of the results of this test it is concluded that aluminized corrosion resisting steel resists corrosion in marine atmosphere equally as effectively as straight, titanium-bearing 20-10.

Wet and Dry Corrosion: Fig. 14 shows the condition of the metal after having been exposed for 11 months to a wet and dry corrosion test. Prior to photographing, all loosely adherent fouling which had accumulated on the specimens was washed off under running tap water. At several points, firmly attached to the surface of photographed specimens 7, 9, and 11, there may be seen blisters of hard, inert matter compounded with rust. Contrary to expectation, no evidence of corrosion attack was discovered under the incrusted deposits. In order to facilitate surface inspection and to determine weight losses accurately, all tightly adherent matter was loosened from the surface of each specimen by immersion in concentrated nitric acid for 8 hours. Macroscopic examination of the cleaned specimens under a magnification of 7 diameters failed to reveal any

evidence of pitting or progressive corrosion. The loss in weight caused by wet and dry corrosion was found to be as follows:

Specimen No.	1	7	9	10	11
Weight before	284.211	281.726	277.272	273.685	275.247
Weight after	284.178	281.673	277.193	273.683	275.189
Loss in grams	0.033	0.053	0.079	0.002	0.068

The data are obviously too scanty to permit the making of a definite statement regarding the relative resistance to corrosion to wet and dry conditions of straight, titanium-bearing and aluminum-titanium corrosion resisting steels.

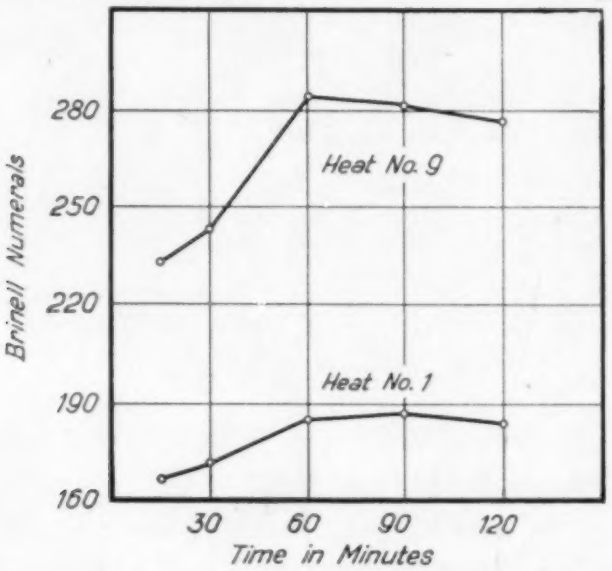


Fig. 10—Showing the Influence of Holding Time on the Brinell Hardness. All Specimens Quenched in Water from 2300 Degrees Fahr.

Oxidation: The susceptibility of Heats 1 and 9 to "wriggles," a kind of intergranular attack having a chicken wire pattern, was also investigated. Two specimens from Heat 1—one forged and the other cast—and one specimen from Heat 9 were scaled and descaled five successive times in the manner outlined under the heading, Corrosion Tests and Specimens. The specimens of both heats, as may be seen in Fig. 15, were comparatively smooth and free from wriggles. The amount of metal lost by each specimen after the five exposures to acid and heat was:

	Cast Specimen 1	Forged Specimen 1	Cast Specimen 9
Weight before	306.714	332.989	322.758
Weight after	298.982	326.864	307.504
Loss in grams	7.732	6.125	15.254
Loss in per cent	2.5	1.8	4.7

The high loss of metal by Heat 9 is not indicative of a lower resistance to oxidation at 1950 degrees Fahr. (1065 degrees Cent.) but is due to the greater attack of the acid pickling solution on the metal. It will be noted that no attempt was made to separate scaling from pickling losses. The figures represent the sum of the two.

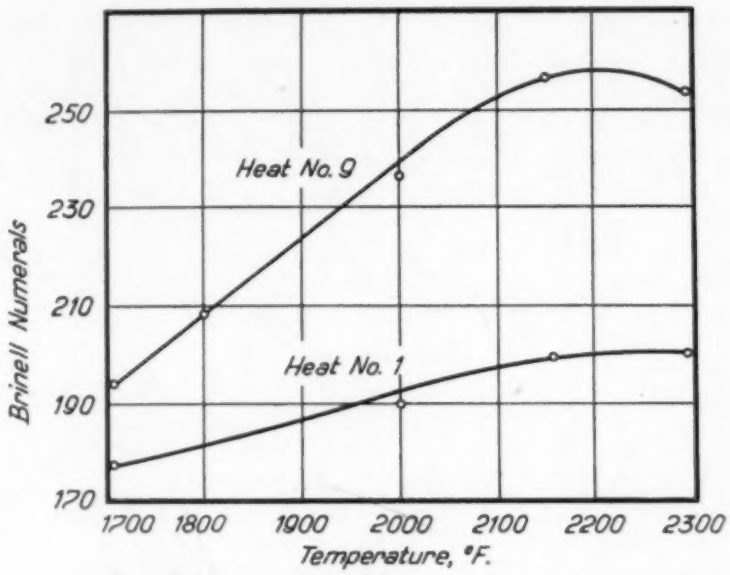


Fig. 11—Showing the Effect of Quenching Temperature on Brinell Hardness. All Specimens Held 1 Hour at Temperature.

Nitric Acid: The total corrosion losses after exposure to 67 per cent chemically pure nitric acid for three 48-hour periods, on specimens quenched from 2000 degrees Fahr. (1095 degrees Cent.) in water, were found to be as follows:

Specimen Number	Total Loss Grams	Penetration Inches per Month
1	0.0216	0.00087
2	0.0178	0.00073
7	0.0203	0.00081
9	0.0147	0.00054
10	0.2859	0.01005
11	0.0863	0.00321

Examination of these figures will suffice to detect that too much aluminum in 20-10 chromium-nickel alloys tends to lower their resistance to corrosion in nitric acid. This is possibly due to the presence of alpha-delta ferrite which is generally believed to be less resistant to acid than gamma iron. Specimens 9 and 11 resisted attack more effectively than specimen 10, probably because of their higher silicon content. Only two specimens, 10 and 11, corroded at

a rate in excess of 0.004 inch penetration per month, the deadline rate of many specifications.

Pit Corrosion in Ferric Chloride: As stated elsewhere in the paper, relative susceptibility to pit corrosion was tested by submerging 1-inch spheres, made from Heats 1, 9, and 10, in 80 cubic centi-

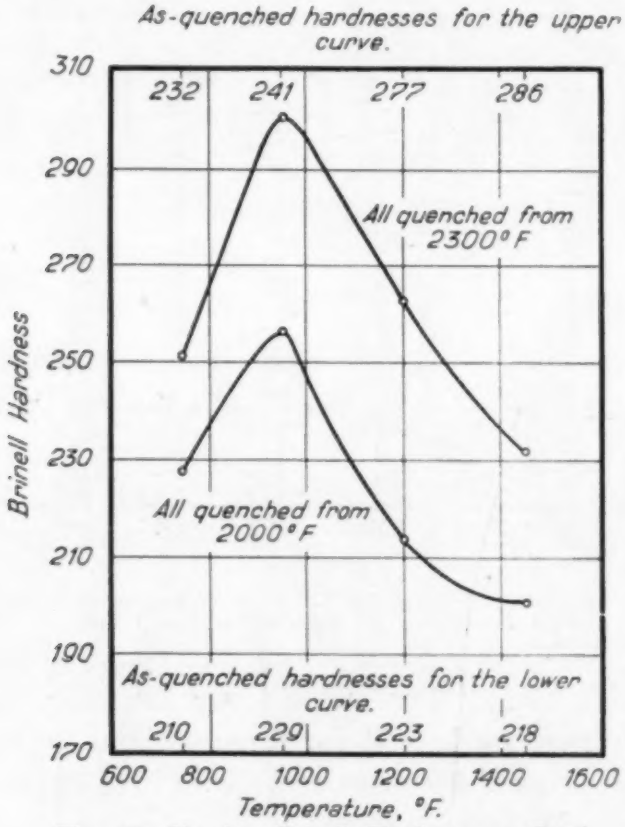


Fig. 12—Showing Brinell Hardness on Specimens Made from Heat No. 9 After Aging at Indicated Temperatures. All Specimens Were Held at Temperature for 8 Hours.

meters of quiescent ferric chloride solution contained in beakers of 200 cubic centimeters capacity. As an absolute quantitative test for susceptibility to pitting, the beaker method of testing is admittedly not as reliable as the highly perfected jacketed U-tube test of H. A. Smith;[7] but for comparative studies, despite some of its alleged drawbacks, the test is capable of yielding fairly accurate and reproducible results. Fig. 16 is illustrative of appearance of ferric chloride pits. They are bottle-neck in shape, and they pierce their way through the metal with an undercutting action that damages the surface but slightly.

[7]Howard A. Smith, "Pit Corrosion of Stainless Steel," METAL PROGRESS, June 1938, p. 597.

In the following tabluation are presented the results obtained with the beaker method of testing. The weight losses and number of large pits are given for two test periods, one of 4 hours and the other of 6 hours duration.

Specimen Number	Initial Weight Grams	Surface Area Sq. Cms.	Weight Losses After 4 hrs. Mgs.	Weight Losses After 6 hrs. Mgs.	No. of Large Pits After 4 hrs.	No. of Large Pits After 6 hrs.
1	75.6028	22.05	59.6	100.1	106	188
9	58.0521	18.68	154.0	198.6	92	154
10	64.3626	19.48	73.0	103.0	19	33

A few points of interest in the above table should be especially noted.

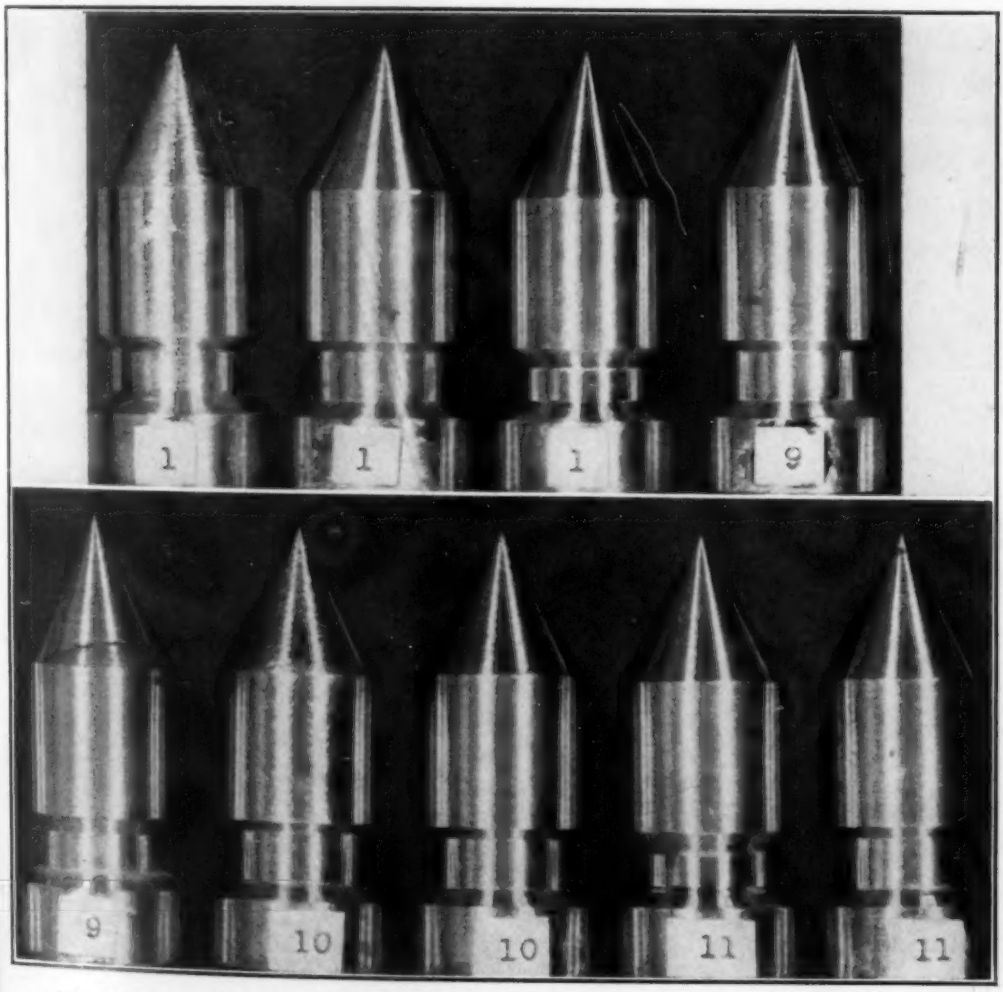


Fig. 13—Corrosion Resisting Steel, Treated with Double Additions of Aluminum and Titanium, After 1000 Hours in 4 Per Cent Sea Salt Spray.

1. The order of decreasing resistance to pitting of the three compositions tested is, 10, 9, 1.

2. High aluminum-titanium Heat 9 suffered the heaviest general overall attack. This is probably traceable to the high titanium content.[7]

3. Pits enlarge in size with time of immersion in the corroding



Fig. 14—Appearance of Specimens After 11 Months Exposure to Corrosion in a Wet and Dry Box. Natural Size.

solution. The size of the pits in the last column is larger than that of those in the 4-hour column.

4. Summarizing the experimental data presented in the table, it is stated that aluminum tends to stabilize the surface of corrosion resisting steel against localized attack in ferric chloride solutions.

Summary

A summary of the more important results of this work follows:

1. Using the equipment, materials, and methods described, the manufacture of corrosion resisting steel under an Al_2O_3-CaO slag results in the incorporation of some incidental aluminum in the metal, the amount seldom exceeding 0.15 per cent.

2. The above initial incidental pick-up of aluminum is frequently reduced from 0.15 per cent to a final average value of 0.10 per cent when the rutile-aluminum addition has been made.

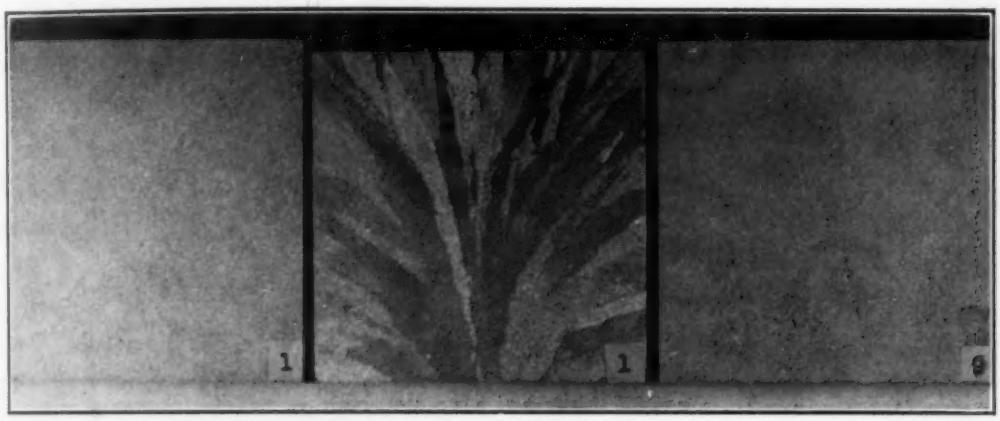


Fig. 15—Showing the Appearance of Specimens from Heats 1 and 9 After Having Been Scaled at 1950 Degrees Fahr., and Descaled in 50:50 HCl, Five Times. Center Specimen and Specimen 9 are Cast; the Other Specimen is Forged. Natural Size.

3. Incidental aluminum affects advantageously both the mechanical and corrosion resisting properties of 20-10 chromium-nickel alloys.

4. Deliberate additions of aluminum, when made in amounts ranging from 0.20 to 3.25 per cent, exert the following effect upon the mechanical properties:

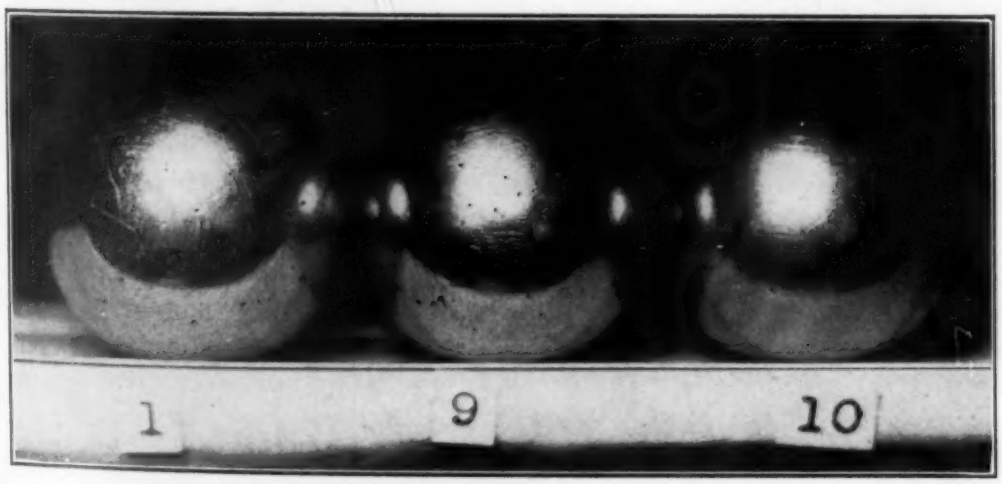


Fig. 16—One-inch Spheres, Showing Pits After 6 Hours Exposure to 10 Per Cent Ferric Chloride Solution.

(a) Tensile strength, proof stress, and hardness are increased continuously up to approximately 3.25 per cent aluminum, while the

ductility is affected adversely—dropping off gradually up to about 1.75 per cent aluminum, and very rapidly from 1.75 to 3.25 per cent aluminum.

(b) High additions of aluminum (over 1.00 per cent) impair seriously the Izod impact strength of the metal.

(c) Excellent combinations of useful strength, toughness, and endurance limit are secured with 1.25 to 1.50 per cent aluminum.

(d) The strength-weight ratio, based on proof stress (0.0002 inch set in 2 inches), is raised from 3.9 for incidental aluminum-bearing Heat 1 to 6.5 for 1.76 per cent aluminum Heat 10. This ratio for Heat 10 is raised still higher, to 7.3, when it is age-hardened.

5. Some of the foregoing effects of aluminum upon mechanical properties are directly traceable to its ferrite-forming as well as its grain-refining tendencies.

6. The influence of aluminum on the resistance of the metal to attack by various corrodents may be summarized as follows:

(a) Resistance to corrosion in 4 per cent sea salt fog and in weak brine solutions is believed to be equal to that of straight 20-10 corrosion resisting steel.

(b) While aluminum does not decrease resistance to corrosion in sea salt spray, it does lower the resistance of the metal to attack by nitric acid.

(c) The addition of aluminum creates a particular resistance to ferric chloride pitting solutions.

7. Heat 9, containing 1.24 per cent aluminum, is age-hardenable; the critical age-hardening temperature appears to be 950 degrees Fahr. (510 degrees Cent.).

Acknowledgments

In closing, the writer wishes to express his appreciation to F. B. Anderson, who supervised the melting of the various alloys; and to T. N. Armstrong, of the International Nickel Company, for the fatigue tests.

DISCUSSION

Written Discussion: By C. E. Sims, research metallurgist, Battelle Memorial Institute, Columbus, Ohio.

Mr. Duma has obviously attained his first objective, which was to evaluate the effect of incidental aluminum contents on a 20-10 corrosion resisting steel

and has shown that such small quantities of aluminum are beneficial to both the mechanical and chemical properties of the steel.

In these steels it is apparent that aluminum has stepped out of its common role as a deoxidizer for steel, and the effects noted are almost wholly those of an alloying agent. This is exemplified in the effect on grain size. We have become accustomed to thinking of aluminum refining the grain of steels because of an effect of certain products of deoxidation. The grain refining action in the present case, however, seems to be due to the persistence of ferrite which acts as an effective barrier to austenitic grain growth. The higher the aluminum content the more ferrite there is and the finer is the grain size.

The action of aluminum in shifting the position of the gamma loop and causing the retention of ferrite is not unexpected because aluminum alone can completely damp out the gamma loop. As Mr. Duma pointed out, the effect of aluminum on the physical properties is probably largely due to the presence of the ferrite.

With this in mind it seems that it would be very interesting to find the effect of the aluminum under conditions where complete conversion to austenite could be obtained. Possibly a higher temperature would do this. The curve for Heat No. 9 in Fig. 11 indicates that some limit was reached at 2200 degrees Fahr. I would like to inquire whether a micro-examination was made of those specimens heated to higher temperatures?

Another method would be to increase the nickel content or decrease the chromium content to allow for the effect of the aluminum. Does the author have any opinions on the probable effect of such adjustments? It seems that the possibilities of improvement with aluminum, already demonstrated, warrant further investigation.

Written Discussion: By H. W. Maack, chief chemist and metallurgist, Crane Co., Chicago.

First, I want to compliment the author on the thoroughness with which he has investigated the effects of aluminum on corrosion resisting steel of the 20 per cent chromium-10 per cent nickel type composition having a small content of titanium. His tests seem to cover all the various properties which might be influenced by aluminum.

With reference to melting practice, we are rather surprised that the practice outlined results in sound stainless steel castings, free from gas holes. We wonder if Mr. Duma attributes sound castings to the use of a Al_2O_3-CaO slag which leaves a small content of aluminum in the steel. In our opinion the loss by oxidation of silicon, manganese and chromium is surprisingly low.

We wonder about the advantage of approximately ¼ per cent of titanium in steel with carbon content of approximately 0.12 per cent. This is a very low content considering the recommended ratio of titanium to carbon content.

With reference to castability, the effects attributed to aluminum are very interesting. In many cases aluminum seems to make molten metal more viscous to pour. The absence of cutting action by aluminum containing steel is to be expected.

All of the photomicrographs shown in the paper contain numerous black spots; those illustrating Heats 10 and 11 are especially densely peppered. The nature of the constituent responsible for these spots is not evident. Are they

holes left by inclusions which have been disloged during polishing, aluminum oxide inclusions, or titanium carbide compound which has not been resolved at the magnification used? It seems that this constituent might exert considerable influence on the impact value, if not the corrosion resistance of the steel.

Written Discussion: By H. A. Smith, metallurgist, Republic Steel Corp., Massillon, Ohio.

It is indeed a pleasure to comment on this very interesting work.

In connection with the aging work, I should like to inquire as to whether any corrosion tests have yet been made on aged alloys and, if so, how the corrosion results compared with results on similar steels unaged. Further, with relation to the usefulness of cast aging alloys, it would be interesting to know whether or not the lower aging temperatures had any tendency to precipitate carbides in Heat 10 not containing titanium but containing 1.76 per cent aluminum and 0.10 per cent carbon.

Referring to the oxidation test, it is inferred that the high loss is attributed to the attack of the metal by the pickling solution (50 per cent HCl at 170 degrees Fahr.) Can it, then, be said that the resistance to attack under this acid condition is less for alloys containing aluminum than for similar alloys not containing aluminum?

Mr. Duma seems to be justified in stating that too much aluminum in 20-10 chromium-nickel alloys tends to lower corrosion resistance in nitric acid. Our experience, however, on wrought alloys not containing aluminum or titanium indicates definitely that silicon above about 0.90 per cent lowers resistance to boiling nitric acid and that, in general, the loss is proportional to silicon content. Further—that the absence or presence of delta iron is not a factor in increasing corrosive attack in nitric acid on wrought alloys not containing aluminum or titanium. Further than this—we are not in a position to comment on the possible causes for the high losses of Heat 10 in nitric acid.

Commenting on the pit susceptibility tests, we feel that paragraph four (4) under the author's remarks, wherein he states that aluminum tends to stabilize the surface of the alloy, would have been much stronger if a heat had been tested for comparison that contained neither titanium nor aluminum. Limited experience on our part does not definitely indicate that aluminum stabilizes the surface of austenitic chromium-nickel alloys in ferric chloride solutions.

We were a little surprised to note that in the type of pit susceptibility test used by the author, there is a general overall attack. In our test with wrought 18-8 low carbon heats containing about 0.50 per cent titanium, no overall attack has been found to occur in ferric chloride of the composition used by the author.

It is noticeable that, for each steel, there are more large pits after a 6-hour than after a 4-hour immersion. I take the figures for the 4-hour period to be the number of large pits equal to or greater than a fixed criterion of size and that after six hours some of the smaller pits existing at a 4-hour period had increased in size in two more hours to the status of large pits—while the large pits at the 4-hour period are now larger. We have found, in the circulating pool method of testing, that all of the pits that will ever form have already done so at the end of, at most, a half hour but that various pits continue to increase in size with time and that the above situation, assumed

for the quiescent immersion of balls, might very well exist. On the other hand—the quiescent immersion might easily give rise to the formation of secondary pits initiated by corrosion products oozing from pits formed earlier. I would appreciate the author's comments on this matter.

As far as the data presented may allow, can we not say—tentatively—from the results of the salt spray, alternate immersion and ferric chloride pit test that titanium additions render these alloys somewhat more susceptible to attack in chloride solutions and that the addition of aluminum may act to minimize the detrimental effects of titanium?

In a spirit of constructive criticism, I am sure the author will allow me to remark that if a heat had been included containing neither titanium nor aluminum—a number of questions concerning aging, physical properties and corrosion resistance could have been more completely answered.

Author's Reply

The author appreciates the comments submitted by Messrs. Sims, Maack, and Smith, and will endeavor to answer the questions which they have asked.

Mr. Sims' discussion is both interesting and instructive. The author regrets that he cannot answer his query regarding the effect of aluminum under conditions where complete conversion to austenite is obtained. Since the writing of this paper, a 75-pound pot of metal was made and poured into test bars. The charge consisted of—

68.0 pounds 20-10 CRS scrap
5.5 pounds Electrolytic nickel
1.5 pounds Aluminum

After a 2000 degrees Fahr. water quenching treatment the following average physical properties and microstructure was obtained:

T.S.	Y.P. (Dividers)	Elong.	R.A.	Microstructure
78,000 psi	41,500 psi	32.0%	28.0%	Austenitic

In connection with the above, it is pointed out that the heat was a crucible and not an electric one, that the flux and slag reactions differed considerably in each case, and that no chemical analysis was made to find how much of the aluminum had been incorporated into the metal.

A micro-examination of specimens made from Heat No. 9, and heat treated to 2200 degrees Fahr., showed a duplex structure. Instead of etching rapidly, and with pronounced darkening of the ferrite, the specimens stubbornly resisted etching and no darkening of the ferrite was observed. The specimens reacted strongly to a magnet.

With regard to the comments by Mr. Maack, it is stated that the production of sound, gas-free castings is attributable to the use of a rather limited amount of slag, to the deoxidation capacity of aluminum, and finally to the practice of thoroughly killing the heat with titanium via the rutile-aluminum addition before any alloying addition of aluminum is made. The metal is

very susceptible to gas hole formation when in contact with damp materials such as incompletely dried out ladles and molds.

It is not necessary to use the recommended ratio of titanium to carbon in steels whose physical make-up is adequately stabilized with high amounts of chromium and nickel. The chief advantage derived from the use of titanium was the obtainment of denser, sounder, and more completely degasified metal.

In regard to the particles in the microstructure of the higher aluminum steels, they are a titanium carbide compound standing in relief, and therefore out of the plane of focus used to photograph the structure. They do impair impact and ductility properties when they are found segregated in the grain boundaries of the material. Their effect upon the resistance of the steel to the action of salt spray is not deleterious.

The discussion by Mr. Smith is most interesting. The only corrosion test which the author made on the aged alloys was boiling them for 72 consecutive hours in the following solution—

$CuSO_4 \cdot 5H_2O$	3 g
H_2SO_4 (sp.gr. 1.84)	10 ml
H_2O (distilled)	87 ml

and then bending them 150 degrees around a pin having a diameter 1½ times the thickness of the specimen, with the following results:

Heat No.	Heat Temp. Deg. Fahr.	Treatment Hold Minutes	Cold Bend Degrees	Condition of the Tension Side
2	950	360	150	OK
5	950	360	150	OK
10	950	360	45	1 sharp crack; remainder of surface smooth.
2	1250	15	150	OK
5	1250	15	150	Slight disintegration.
10	1250	15	30	Entire surface replete with numerous cracks.

With respect to the network type of cracking which is characteristic of carbide precipitation, the 1250 degrees Fahr. treatment inflicted the severest damage on the high aluminum heats. With respect to the type of brittleness which manifests itself in a single cleavage plane, the 950 degrees Fahr. treatment was most damaging.

Mr. Smith was surprised at the overall attack noted in the author's pit susceptibility test. The overall attack made itself manifest by lightly etching and thereby faintly bringing out the cast structure of the metal. Regarding the relation between the size, number of pits, and time of immersion in the pitting solution, this was found to be the same as that noted by Mr. Smith in the circulating pool method of testing. Enlargement of pits was only noted. No new pits appeared even after 10 hours of exposure.

A NEW METHOD FOR THE RAPID DETERMINATION OF CARBON IN SAMPLES OF PLAIN CARBON OPEN-HEARTH STEEL

By B. A. Rogers, Karl Wentzel and J. P. Riott

Abstract

A new method has been developed for the determination of the amount of carbon present in samples of plain carbon steel taken from the open-hearth furnace. This method depends upon the measurement of the coercive force of small ingots of killed metal poured from a sampling spoon. The magnetic measurements are made in a coercimeter which is a very simple device for determining this particular magnetic property. In practice it is sufficient to measure the coercive current and in this report the relationship between coercive current and carbon content is shown by means of a graph.

THE need of those engaged in operating open-hearth steel furnaces for a rapid method of determining the carbon content of samples taken from the molten metal has already resulted in the development of two non-chemical methods for this purpose. Of these, one involves the measurement of electrical resistance[1] and the other[2, 3] depends primarily upon the magnetic permeability of the sample. It is the object of this paper to describe a third method, based on the determination of the coercive force of cast samples.

For the present purpose, the coercive force of a piece of steel may be defined as the intensity of the magnetic field that must be applied in the direction opposite to that in which the specimen was originally magnetized to reduce the magnetic flux to zero. The measured value of coercive force depends upon whether the total flux due to both the specimen and the field of the demagnetizing coil

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[1]C. Holthaus, Die Bestimmung des Kohlenstoffgehaltes im Stahl durch Messung des Elektrische Widerstandes: Ber. Fachausschüsse Ver. deut. Eisenhüttenl., *Chemikerausschuss,* Ber. 39, November 1922.

[2]Paul Klinger and Herbert Fucke, Die magnetische Schnellbestimmung des Kohlenstoffs im Stahl mit dem Karbometer von Malmberg: *Archiv Eisenhüttenw.*, Vol. 3, November 1929, p. 347-352.

[3]Gilbert Soler, "New Carbometer Controls Speed Production and Improves Quality," Metal Progress, Vol. 31, 1937, p. 159-162.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The authors are associated with the Metallurgical Division, United States Department of the Interior, Bureau of Mines. Manuscript received June 24, 1938.

or only that part contributed by the specimen is reduced to zero. In the present instance, the choice made is not important, for the difference between the two values is negligibly small.

The technical literature does not appear to contain any mention of an investigation of the relationship between coercive force and carbon content of cast steel. Several individuals[4, 5, 6, 7] have concerned themselves with such studies on fabricated rods and have presented data showing a correlation between these properties, but in each case the number of samples was small, and furthermore, the results obtained by different investigators do not show a satisfactory agreement. Probably many individuals engaged in studying magnetic materials consider the connection between coercive force and carbon content to be of a qualitative nature only.

Some Features of the Testing Apparatus

A number of devices are available for determining the coercive force of bar samples. Of these, the coercimeter was selected as being the most suitable for the problem on account of the simplicity of the apparatus and the ease of operating it. An apparatus that was essentially a coercimeter was used by Madame Curie[8] forty years ago, but the device was not put to much use until recently.[9, 10, 11, 12] Because previous accounts have described the instrument quite fully, a general discussion is unnecessary. However, it may be worthwhile to point out a few special features of the model, which was finally developed after considerable experimentation.

These features and the reasons for employing them can be most conveniently understood with the aid of the diagram exhibited in Fig. 1. This figure is divided into two areas by the dotted line *xy*, which passes through the symbol for the 12-volt storage battery.

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[4]Mme. Curie, Sklodowska, "Propriétés Magnetiques des Aciers Trempes," *Bulletin*, Société Encouragement Ind. Nat., Series 5, Vol. 3, 1898, p. 36-76.

[5]E. Gumlich, "Magnetic Properties of Iron-Carbon and Iron-Silicon Alloys," *Transactions*, Faraday Soc., Vol. 8, 1912, p. 98-114.

[6]Carl Benedicks, "Recherches physiques et physico-chimiques sur l'acier du carbone," Upsala, Librairie de l'Université, 1904, p. 166.

[7]E. D. Campbell and G. W. Whitney, "The Effect of Changes in Total Carbon and in the Condition of Carbides on the Specific Resistance and on some Magnetic Properties of Steel," *Journal*, Iron and Steel Institute, Vol. 110, 1924, p. 291-311.

[8]Mme. Curie, Sklodowska, work cited (footnote 4).

[9]Hans Neumann, Das Koerzimeter: *Archiv Tech. Messen*, Vol. 4, 1935, p. T64-T65.

[10]C. W. Davis and Max Hartenheim, "A Simple Method for the Determination of Magnetization-Coercive Force, *Rev. Sci. Inst.*, Vol. 7, 1936, p. 147-149.

[11]R. S. Dean and Charles Y. Clayton, "The Mechanism of Steel Hardening and Tempering as Indicated by Coercive Force Measurements," Transactions, American Society for Metals, Vol. 26, 1938, p. 237-252.

[12]C. R. Austin and R. S. Norris, "Effect of Tempering Quenched Hypereutectoid Steels on the Physical Properties and Microstructure," Transactions, American Society for Metals, Vol. 26, 1938, p. 789.

The lower of these areas shows the electromagnet used for magnetizing the specimen in preparation for measuring its coercive force. The coercimeter in which the measurements are made is represented schematically in the upper area.

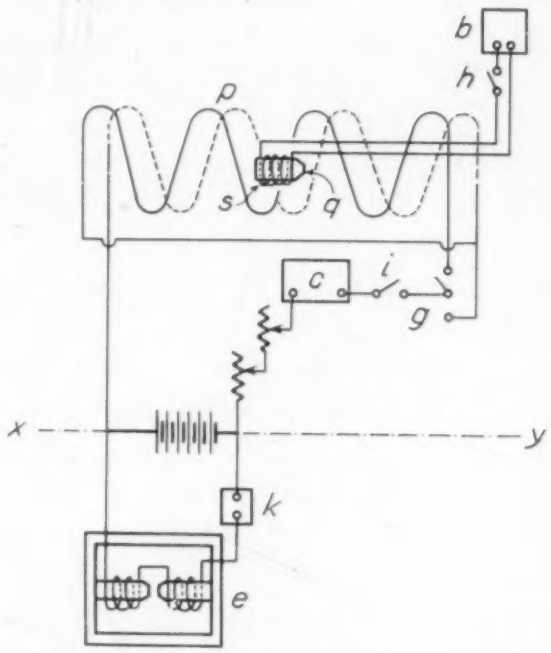


Fig. 1—Circuit Diagram of the Portable Coercimeter Test Set.

b—galvanometer
c—ammeter
g—switch for doubling range of coercimeter
h—switch for closing secondary circuit
i—switch for applying power to primary circuit
p—primary windings of coercimeter
q—specimen
s—secondary winding of coercimeter
e—electromagnet for magnetizing specimen
k—circuit breaker

With respect to the lower area, two features are of interest: First, one pole piece of the electromagnet "e" is provided with a movable core, which is forced out into the gap under the action of a spring. This arrangement holds the specimen in place and assures satisfactory magnetic contact for samples of slightly different length. Second, the circuit breaker "k" guarantees that the magnetizing current is interrupted at approximately the same speed in all cases, a characteristic for which the desirability will appear shortly. The sample may be removed from the magnet either while the current is still flowing or after breaking the circuit. The former procedure requires considerable physical effort, chiefly because the magnetic force holds the movable core very tightly against the sample.

It has been known for some time that the rate of decrease of the magnetizing field affects the final state of magnetization of the sample.[13] Neumann[14] mentions certain procedures which take this fact into consideration. Our own experiments demonstrated that if the operator always jerked the specimen out of the gap with all the force possible, the state of magnetization could be readily duplicated in successive trials. (This method was used in making the measurements from which Fig. 3 was plotted). However, two individuals of different muscular power do not produce similar states of magnetization in the sample, and for this reason it was decided to adopt the practice of cutting off the current before removing the sample from the electromagnet. To insure that the magnetic field decreased at the same rate in all cases, the circuit breaker was incorporated into the circuit so that by tripping it the same type of current interruption would always occur. It should be added that with either procedure the magnetic field was reversed several times during the magnetization process by means of a reversing switch not shown in the diagram.

The essential elements of the coercimeter pictured in the upper area are the primary winding "p" and the secondary coil "s". When current is passed through "p", a magnetic field is built up which tends to demagnetize the specimen "q". The secondary coil can be displaced axially from a position where its geometric center coincides with that of the specimen to a point beyond the influence of the latter. When such a motion is made, the galvanometer to which this coil is connected will register a deflection unless the demagnetizing field has been increased to a value just sufficient to produce zero magnetization of the specimen; that is, to a value equal to the coercive force.

In the particular model being described, the switch "h", which is used to close the galvanometer circuit when a reading is being taken, is mounted on the handle by which the coil is moved. This arrangement permits opening or closing the secondary circuit at will and at the same time leaves one hand free to adjust the rheostats which control the demagnetizing current. The primary winding is composed of two layers, so connected that by operating switch "g" either the inner one alone or both of them can be thrown into the circuit. By the use of a double winding the instrument is not re-

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[13]A. von Waltenhofen, "Ueber den magnetischen Rückstand im Eisen," *Ann. Phys. Chem.*, Vol. 120, 1863, p. 650-653.

[14]Hans Neumann, work cited (footnote 9).

quired to carry such heavy current when samples with a high coercive force are being measured, and rheostats of smaller range may be used.

Laboratory Investigation

The investigation of the relationship between coercive force and carbon content included experiments both in the Bureau of Mines laboratories and in steel plants. The earliest experiments were conducted at the Homestead plant of the Carnegie-Illinois Steel Corporation under arrangements made through the courtesy of M. W. Lightner, chief metallurgist of this plant. In spite of the fact that every facility was made available by the personnel of this plant, we were unable to obtain consistent results. It was therefore decided to return the apparatus to our own laboratory for further study of the technique of taking and testing samples. The procedure developed and the results obtained in these laboratory studies will now be described.

Experimental Procedure

In outline, the process of taking and testing samples is simple: A spoonful of the metal is killed with a considerable quantity of aluminum rod and poured into a split mold especially constructed for the purpose. As soon as the top has solidified, the mold is opened and the little ingot allowed to drop into the cooling medium. A specimen of the desired length is then cut or broken from the bottom of the ingot, magnetized, and placed in the coercimeter for testing. Actually, a certain amount of experimentation was involved before a satisfactory technique was attained.

The melting operation was carried out with a high-frequency furnace, using magnesia crucibles with a capacity of 12 to 15 pounds of molten steel. Although it was believed that moderate amounts of alloying elements would be unlikely to affect the magnetic data, the precaution was taken of using Armco ingot iron as melting stock and adding pieces of Acheson graphite electrode to bring the carbon to the desired percentage. Since to pour the metal directly from the furnace into the mold would not have allowed opportunity for the addition of aluminum, and the method of dipping a small spoon into the crucibles was impractical because of the mechanical conditions, the practice was adopted of pouring the metal first into a spoon and

filling the mold from this. Excessive cooling of the approximately 2 pounds of metal during transfer from the crucible to the mold was avoided by having the bowl of the spoon, which was kept coated with

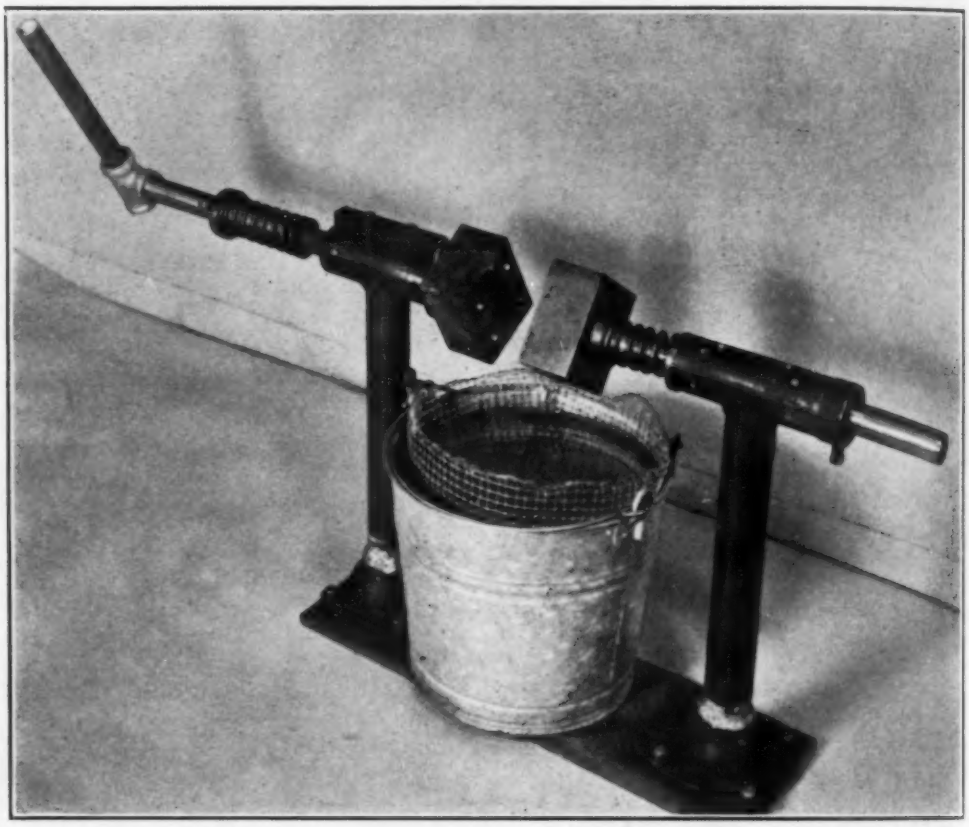


Fig. 2—The Mounting for the Molds.

a layer of alundum cement, preheated to about 1000 degrees Cent. (1830 degrees Fahr.) in a gas-fired furnace. The aluminum was added in the form of ¼-inch diameter rod. To insure the addition of the desired amount of this element into the steel, a section of the proper length was attached to the end of a soft iron wire so that it could be thrust under the surface of the molten metal.

During the laboratory studies it was found advisable to change the mechanism for holding the two halves of the mold together to eliminate occasional trouble in stripping the ingots promptly. A simple mounting was constructed such that by turning a handle the mold was inverted and the two halves separated, allowing the sample, 5 inches in length by ⅝ inch in diameter, to fall out. Fig. 2 shows the apparatus used in the plant studies and illustrates a mounting of this type. A quenching device was made in which water flowed upward

through a rather large funnel mounted within a containing vessel. When the samples fell from the mold into this funnel, they slid down to the center and were cooled by the upcoming current of water. The temperature of the water as it came from the mains was fairly uniform over the period of the investigation. Because the variation which may be produced by differences in the temperature of the water was not fully appreciated at the time, accurate records were not kept but the temperature probably did not vary much from 13 degrees Cent.

In the beginning of the investigation, magnetic measurements were conducted upon two different lengths of samples. One type was about 3 inches long and the other, 1⅜ inches. Both lengths of specimens were cut from the bottom portion of the ingot, the shorter being cut from the bottom of the longer after it had been tested. Cutting was done with a thin disk impregnated with silicon carbide particles. Freedom from annealing effects during the cutting operation was assured by having the sample clamped under water. Measurements on the long specimens were abandoned before completing the investigation because the correlation obtained with them was less satisfactory than was found for the short ones. Since the long specimens could not be inserted in the gap of the electromagnet, they had to be magnetized in the coercimeter itself. With this arrangement a field intensity of 550 oersteds was the maximum obtainable whereas the short specimens could be subjected to a field strength of 3000 oersteds. Apparently, the test pieces must be magnetized practically to saturation if good results are to be obtained, and this condition is probably not reached at the lower field strength. The electromagnet used for the short specimens was designed for operation on a 110-volt d.c. circuit. It was capable of producing a field of 7000 oersteds in its 1⅜-inch gap, but less than half this strength was required to produce practical saturation of the samples.

Drillings for carbon analysis were taken either from the short specimen actually tested or from the part that had been immediately adjacent to it. The analyses were conducted by the method of combustion in oxygen. A standard sample of the type supplied by the National Bureau of Standards was used at frequent intervals to check the accuracy of the apparatus.

Results

All of the data taken upon the short samples are condensed in

Fig. 3, which shows the dependence of coercive force upon carbon content for the four heats made after a satisfactory scheme of handling the samples had been developed. Of the 28 samples taken during these four heats, 27 are represented on the graph. The remaining one, from heat N, was discarded because it stuck in the mold, an event that was known from previous experiments to cause the coercive force to decrease. Upon the whole, the correlation is

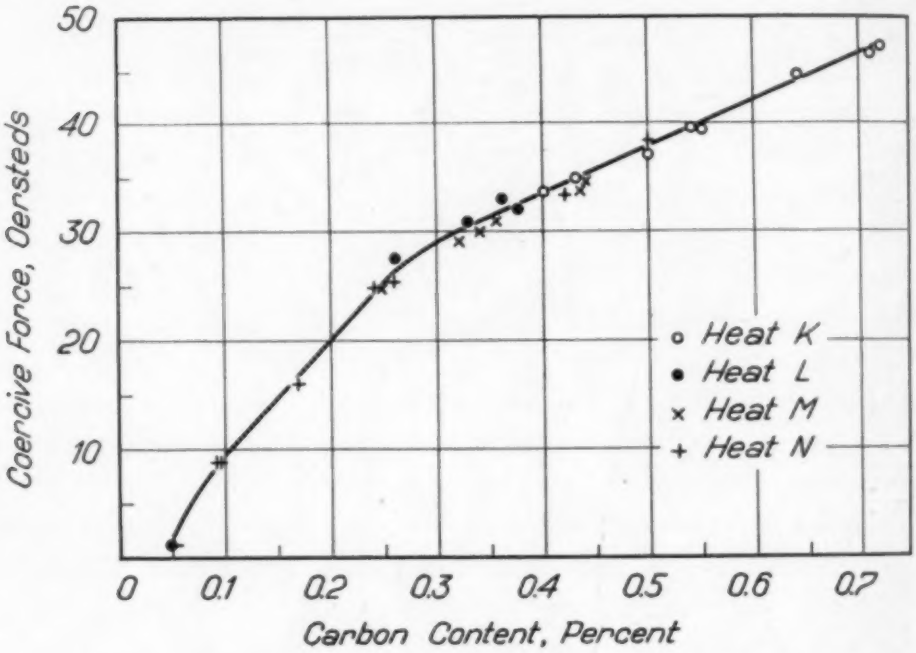


Fig. 3—Coercive Force-Carbon Content Curve for Steel Samples Cast in the Laboratory.

satisfactory. Most of the points are within 0.01 per cent, and only two of them lie farther than 0.02 per cent carbon from the curve. It is of interest to note also that some of the points represent samples to which were added ½ inch of aluminum rod rather than the customary 2 inches. Apparently, the percentage of aluminum to be added is not very critical, provided that the sample is completely killed.

The Plant Investigation

The satisfactory results that had been attained warranted the acceptance of an invitation to try the equipment at the Steubenville (Ohio) plant of the Wheeling Steel Corporation. As this plant produces, principally, low carbon steel containing relatively low per-

centages of alloying elements, it offered favorable conditions for the trial of such a method of determining carbon.

The Experimental Procedure

Before beginning work in this plant, the previously described portable coercimeter test set and electromagnet were constructed. A few check tests between this equipment and the laboratory apparatus revealed a difference amounting to several per cent in the values of coercive force obtained. However, this disagreement between the two test sets was not deemed important because the success of the method depends on the consistency of a given apparatus rather than the determination of the exact value of coercive force.

A number of changes were made in the sampling equipment also. The period of time necessary to cut off the lower portion of the ingot with the abrasive wheel was undesirably long, and furthermore the apparatus was not easily portable. The mold was therefore provided with a constriction so placed that the resulting groove in the ingot would be correctly located for breaking off the specimen. This is the mold pictured in Fig. 2. A satisfactory device for holding the ingot for breaking was made by drilling a suitable hole in a solid block of steel. When the ingot was thrust into this hole until the groove was flush with the side of the block, a sharp blow with a heavy hammer sufficed to break off the unused portion. To avoid scarring the polefaces of the magnet, the roughness of the fractured end of the specimen was smoothed off a little on a grinding wheel. Portable quenching apparatus was provided by the pail and wire-gauze container pictured in Fig. 2. As soon as the ingot fell into the gauze vessel, the latter was moved about vigorously in the pail to bring cool water in contact with the hot metal. No special equipment was required to take the sample of metal from the furnace since the ordinary sampling spoon was quite suitable. The spoon was coated with slag in the usual way before dipping it into the bath. When the sample was obtained the spoon was rested on the floor for a moment while the slag usually present was pushed aside with an iron rod and a 2-inch length of aluminum rod was thrust into the metal. After a few seconds had been allowed for the aluminum to diffuse through the steel, the metal was poured into the mold until a small head or button appeared in the funnel portion.

Upon beginning work with the equipment just described, diffi-

culty was encountered in getting consistent results, particularly in the lower carbon range. Various schemes, such as holding the ingots for a definite period on an asbestos board before dropping them into the quenching water and the employment of a soap solution for quenching purposes were tried without success. Because of the failure of these various devices to improve the situation and also because there was some inclination of the samples to stick in the mold, it was decided to substitute the smooth mold that had been employed in the laboratory investigation. As some of the results appeared more promising after this change, a device was constructed for grooving the ingots so that the specimens could be knocked off in the same manner as when the constricted mold was used. The substitution of a thin cutting disk for the grinding wheel of a small bench grinder gave a very satisfactory apparatus for this purpose. By using a simple guide, no trouble was experienced in cutting a groove of the required depth in 15 to 60 seconds, depending on the percentage of carbon in the ingot. Furthermore, it was found that less smoothing was required than for the ingots with the cast-in groove. Under these circumstances, although it was believed that a constricted mold could be made to give satisfactory results, there was little inclination to return to this type.

The next progressive step was to control the temperature of the water more closely. A temperature of 21 degrees Cent. was selected as fairly satisfactory for year-round operation. Water colder than this can easily be warmed with a piece of hot metal and whenever the water in the mains exceeds this temperature a refrigerated supply is generally available. When taking more than one sample at a time, it was found convenient to have three pails of water handy so that additions of warmer or cooler water could be made. The adjustment of water temperature usually required about a minute. The temperature of the mold was not maintained at a particular value. It was generally too warm to permit continuous contact with the hand and not hot enough to produce a sizzling effect when water was thrown upon it.

The use of the smooth mold and controlled water temperature appeared to give satisfactory results when the ingots were dropped into the water immediately after solidification. This method was therefore followed to obtain samples from a number of heats of steel. Further experience with the method of taking and testing samples described in the previous paragraphs demonstrated its suitability with

respect to speed of operation. The total interval between pouring the sample and completing the test need not exceed five minutes. Furthermore, the apparatus is not expensive to make and does not appear to be sensitive to vibration. Probably a simpler arrangement for clamping the mold shut could be used with equally satisfactory results.

Results

During the plant investigation, determinations of coercive current and carbon content were made on samples from sixteen heats of open-hearth steel. To analyze these data, the values of coercive current (current required to demagnetize the specimen), which serve the purpose quite as well as the figures for coercive force, were plotted against the corresponding percentage of carbon. An inspection of the finished graph, which is not exhibited because of the confusion that would arise from reducing such a chart to appropriate size, revealed that a satisfactory correlation existed. To illustrate the results, Fig. 4 has been prepared from the data for five representative heats. In this figure, the separate points are readily distinguishable, and the position of the mean curve is the same as if all the points had been included.

The mean curve consists mainly of two straight lines which intersect at 0.23 per cent carbon. It is not certain that the change of slope in this locality is as abrupt as has been indicated, but the line drawn appears to represent the conditions as accurately as any which might be used. Furthermore, examination of Fig. 3 shows that the curve pictured there might readily have been drawn as two straight lines intersecting in the same vicinity. The number of points obtained in the laboratory studies was not sufficient to establish the nature of the curve with certainty, but the numerous data of the plant investigation indicate a very sudden change at about the carbon content indicated. It is interesting that samples which are represented by points above this break experience a noticeable decrease in coercive current within an hour after being cast, whereas specimens corresponding to points on the steeper portions of the curve do not exhibit an observable change in several hours. The number of measurements made was not sufficient to locate the exact point at which the aging behavior altered, but the change occurs somewhere in the vicinity of 0.23 per cent carbon.

The fact that the graph presented in Fig. 4 refers only to samples

quenched directly in water at 21 degrees Cent. should be emphasized. The range of temperature through which the water may vary without affecting the readings of coercive current has not been definitely fixed. Apparently samples which have been quenched in water at 30 degrees Cent. give about the same results as if the colder temperature had

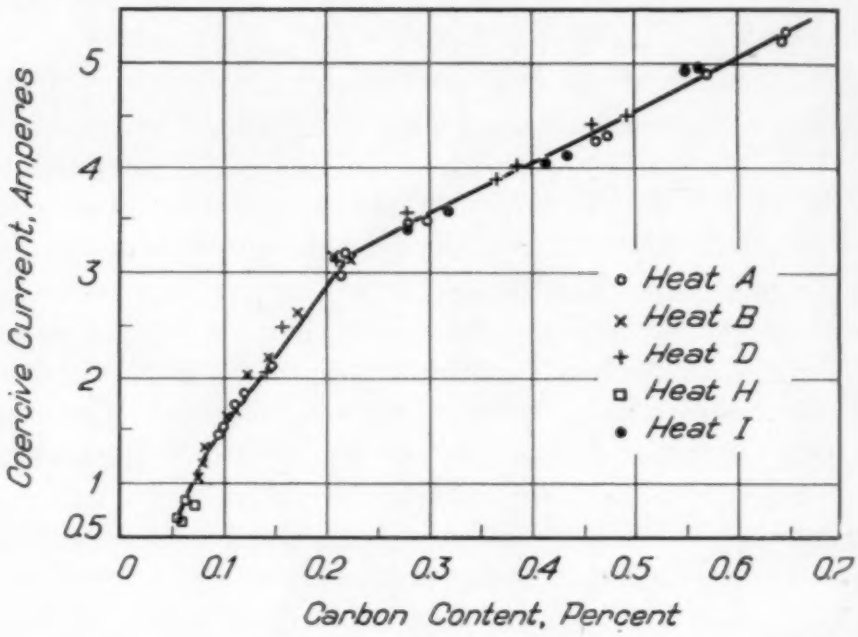


Fig. 4—Coercive Current-Carbon Content Curve for Sample of Open-Hearth Steel.

been used; on the other hand, there is some indication that with a water temperature of 15 degrees Cent., slightly higher readings will be obtained for the same amount of carbon.

Occasionally, samples show readings of coercive current which do not agree with the carbon content as obtained by chemical analysis. There are several causes for these discrepancies. First, the ingot may not drop out immediately when the mold is opened. Specimens broken from such ingots will indicate too low a carbon content. Fortunately, trouble of this kind occurs infrequently and is evident at once. A second, and in these experiments fairly frequent, source of disagreement arises from heterogeneity of the specimen with respect to carbon content with consequent difficulty in calculating the correct average. Samples taken soon after the addition of ore or pig iron constitute the bulk of such cases. It was, of course, anticipated that metal taken after such additions would not be representative of the bath, but this fact in itself was not considered a disadvantage in establishing a relationship between coercive current

and carbon content. However, the opposite ends of some samples showed differences of 0.02 or 0.03 per cent, and a variation of more than 0.05 per cent carbon was observed in more than one instance. Third, specimens which have cavities are likely to give readings which correspond to more carbon than is actually present. Failure to kill the metal properly is one cause for such cavities. In a few cases, the use of 4 inches of aluminum rod appeared advisable. Inclusions of slag were occasionally present, the material having slipped in during the pouring of the ingot. A fourth cause for incorrect readings is mushiness of the metal when poured. This condition, which occurs frequently when the temperature of the steel bath is low, causes the readings to indicate too much carbon. No influence on the results appears to be exerted by copper up to about 0.30 per cent, the maximum tried, or by moderate amounts of manganese. The four reasons enumerated account for all but about a half dozen of the discrepancies noted during the plant investigation. Errors in reading the ammeter, difficulty in sampling caused by carbon segregation, and failure to note mushiness are the most likely causes of incorrect values.

Acknowledgments

It is a pleasure to record the kind co-operation of the personnel of the steel plants in which the authors obtained their samples. The courtesy of Mr. Lightner and others of the Carnegie-Illinois Steel Corporation has been mentioned. Arrangements with the Wheeling Steel Corporation were made through the kindness of F. G. Norris, open-hearth metallurgist. The cordiality of the staffs of both the metallurgical and open-hearth departments made our work there enjoyable. The co-operation of P. D. Cameron, open-hearth superintendent, was especially appreciated. Acknowledgment is also made to the Edgewater Steel Company and particularly to W. J. Reagan for samples not, however, included in the above data. Finally, there should be mentioned the effective assistance of Cresap Moss of our own staff before he was transferred to duties at another laboratory.

DISCUSSION

Written Discussion: By Gilbert Soler, manager of research, Steel & Tube Division, Timken Roller Bearing Co., Canton, Ohio.

Any method or equipment to be used for steel making control by open-hearth operators must be simple and accurate in operation, require very little

maintenance, and must be economical. The method of determining carbon content of steel by measurement of coercive force appears to combine all of these essentials and the authors are to be commended for making a valuable contribution to the steel industry.

The present carbometer fulfills the requirements stated with the exception that the initial investment is high.

In comparing the method described by the authors based on measurement of coercive force of steel samples with the carbometer method which is based on the measurement of magnetic permeability the following points are considered:

(1) *Simplicity and Accuracy*

In both methods samples of molten metal are taken from the bath in the usual manner and killed with aluminum wire. Care must be taken that the test bar is sound and homogenous as errors from this source will result for both methods. Control of the temperature of quenching water is probably more important with the method based on coercive force measurements; and the cutting of the specimen from the cast test bar is an added operation.

Taking of actual readings on the two instruments appears to require equivalent skill and time.

The instrument is not sensitive to vibration which is of some advantage over the carbometer which must be protected from vibration and wide temperature variations.

The accuracy of the two methods appears to be of about the same order.

(2) *Cost*

The authors have stated that the apparatus is not expensive to make and this should be an outstanding feature as the carbometer has a high initial cost. This feature should extend the availability of rapid carbon analysis equipment to operators who have hitherto been unable to afford such equipment.

The writer would like to ask the authors if they feel that with further research this method can be employed for measuring carbon content of alloy steels with suitable corrections being made for residual alloys.

Written Discussion: By H. J. Sweeney, assistant superintendent, Open-Hearth Department, Republic Steel Corp., Youngstown, Ohio.

Dr. Rogers and his associates have advanced what appears to be an exceptionally useful piece of equipment for future open-hearth work. Providing the measurement of carbon by this method proves practical, the cost would appear to allow for the installation of a set of equipment for, say, each two furnaces. The continual knowledge of the carbon content of the bath, resulting from the availability of this equipment close to the furnace, would materially increase the furnaceman's control over the bath and help tonnage output. At present, rapid carbon determinations are available only from expensive machines that must of necessity be protected by installing in a secure location that is not always as convenient to the furnace as is desired.

Several doubtful features of Dr. Rogers' equipment must be determined by actual use on the open-hearth floor. For instance, to be of general use it must not be too sensitive to residual alloy contents in the bath. Again, in prac-

tical open-hearth work, the temperature of the water for chilling the test specimen could probably not be controlled as closely as Dr. Rogers has done in his experimental work.

As previously stated, the above practical problems can only be answered by actual practice in the plant and the possibilities apparently indicated by carbon determination with this method would lead to the conclusion that it should be immediately tried in regular practice by open-hearth operators.

Oral Discussion

E. G. HILL:[35] I would like to know if the author quenches the same for all carbon contents?

B. A. ROGERS: We quench them about eight or ten seconds after pouring, shortly after the ingot has been solidified. The data which were taken were taken without spilling the cone and all carbon content is taken in identically the same way.

A. V. DE FOREST:[36] Any magnetic method is always a good one and I very much hope that this matter can keep on developing to a really practical conclusion. There is one particular hitch that has been mentioned a number of times here, and that is the effect of residual alloys. It has been a universal result of magnetic measurements that they run more nearly parallel with hardness, whatever that is, than they do with almost any other mechanical measurement and I would very much suspect that in this case the results will correlate very nicely with the hardness of the specimen; and in that connection I would beg to inquire if it might not be possible to eliminate the variable quench by allowing cooling of the specimen and then reheating it in an induction furnace to a known temperature and then performing the quench. I have a feeling that the quenching operation is one of the least controlled parts of the whole process. The magnetic measurement can be controlled to any degree of accuracy that anybody needs. One element can replace another and as hardness is not a fixed ratio to a carbon content unless the alloy content is pretty well known we would suspect there would be the same relationship in the coercive force test.

B. A. ROGERS: What is the effect of an alloy and will the instrument work for steels that do contain alloy elements? The only answer which we can make at the present time is that we think we can. We have not had the opportunity to investigate it thoroughly.

Authors' Reply

We quench all samples about 8 or 10 seconds after pouring; that is, just after the top of the ingot has solidified. We have taken samples from which the metal in the cone was spilled but the data presented here were all taken on unspilled test ingots.

We have not yet had an opportunity to try out the instrument on alloy

[35]Director of research, Lukens Steel Co., Coatesville, Pa.

[36]Professor, mechanical engineering, Massachusetts Institute of Technology, Cambridge, Mass.

steels. There is little doubt that the presence of a considerable amount of an alloying element will alter the readings. A modified calibration curve would be required in such a case.

It is difficult to answer Professor de Forest's question about the possible advantage of reheating the specimen to a fixed temperature in an induction furnace since probably only actual trial would give the information and we have not made the experiment. The additional apparatus required would complicate the procedure a little and increase the cost of the equipment considerably.

STRESS-CORROSION CRACKING IN AUSTENITIC STAINLESS STEELS

By S. L. Hoyt and M. A. Scheil

Abstract

This paper summarizes the results of a series of corrosion tests made on different types of austenitic stainless steels. The authors discuss the use of a new test which they have employed to determine the stress-cracking tendencies of the austenitic stainless steels. The test combines heat treatments which may arise from the necessity of heating, forming and welding with stress which may be present in equipment fabricated from these alloys.

Actual formation of open cracks in chemical equipment was studied and laboratory stress-corrosion tests made to duplicate the conditions of service bearing on the tendency towards cracking. Stress-corrosion cracking is shown to be intergranular in nature with the steel stressed and subjected to suitable corrosive conditions, although the susceptibility to intergranular attack is not always sufficient to produce cracking.

This variable behavior is discussed and believed to be due to some quality or characteristic of the steel in the as-received condition.

The authors failed to produce stress cracking in stabilized alloys or with properly quenched austenitic stainless steels.

Introduction

STAINLESS steels are applied extensively to the construction of equipment used in the chemical and allied industries. They are excellent materials for such applications, though inasmuch as this use has already been discussed in great detail in the technical literature, that need not be emphasized here. The fabricator of this equipment is confronted with certain problems of his own and which also concern the performance of the equipment in service, which have

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, S. L. Hoyt is director of research, department of metallurgical research, and M. A. Scheil is research metallurgist in the same department, A. O. Smith Corp., Milwaukee. Manuscript received June 23, 1938.

perhaps not received the attention they deserve. These problems arise from the necessity of heating, forming, and welding the materials because each of these operations may affect the steel and its subsequent behavior. For the past few years the authors have been studying these effects to guide in the choice of steel to be used for vessels and the selection of treatments through which the steel can be safely passed in fabrication. This experience has taught that the steel must be selected not alone to withstand the ultimate service conditions but also to meet fabrication requirements. The corrosive effects which are, or may be, involved in service are numerous and include the various types to which stainless steel is subject. While the authors have considered these effects broadly they have selected for the present discussion that of "stress-corrosion cracking" of the austenitic stainless steels. Failure by combined stress and corrosion is not a very common occurrence yet most users of stainless steel equipment are undoubtedly aware of its possibility. The authors know of some cases which cause but little trouble though they are undoubtedly special. Usually the formation of an open crack in chemical equipment is highly undesirable and hence we have made a special study of this effect in an effort to learn how it is to be avoided in commercial practice. Furthermore, stress-corrosion cracking has not as yet been publicly discussed, insofar as the authors are aware.

Stress-corrosion cracking is intergranular in nature and undoubtedly belongs in the category of effects which originate at grain boundaries. Corrosion cracking of brass and the so-called caustic embrittlement of boiler plate are well known examples, while failure of silver soldered joints and intergranular chemical attack, or "sugaring," are two manifestations of this susceptibility in stainless steel. "Sugaring" is the term used by the authors to mean the well known disintegration of the austenitic steels by progressive chemical attack along the grain boundaries. This effect can be detected by noting the increase in resistance or by bending the specimen and noting the opening up of cracks. It can also be detected in its early stages by probing the surface with a steel point to loosen up the grains and, at a little later stage, by the sandy feel of the surface. Before proceeding to a discussion of our own observations, however, we would point out that susceptibility to intergranular attack is not at all sufficient to produce cracking, though the steel is stressed and subjected to suitable corrosive conditions—some additional factors are undoubtedly involved. Out of quite a number of test samples which

failed by sugaring, only a few showed simultaneous susceptibility to cracking. At present it appears that this variable behavior is due to some quality or characteristic of the steel in the as-received condition.

Service Failures

Our attention was first directed to stress-corrosion cracking by experience with a solid manway neck in a paper pulp digester and this case will be used as an example of a service failure. This unit was used for sulphite digestion and was constructed of the 21-11



Fig. 1—Inside Surface of Manway Neck Showing Cracks. The Top of the Photograph was Originally the Position of the Weld Seam. × ½.

chromium-nickel, Type 307, alloy. The manway neck was made of solid stainless steel ⅝ inch thick. After installation the vessel was tested by being put through 20 cooking cycles with the regular heating and cooling periods but before the actual liquor was placed in the vessel. At this time the vessel was pressure tested and found to have no leaks. Inasmuch as the vessel appeared to be fit for operation the regular charge with sulphite liquor was introduced. After relatively few cooks the manway neck developed cracks which extended out from the junction of the manway and the vessel proper. This resulted in leaks of the liquor and the unit was shut down for a study of the cause of the cracks.

The composition of the rolled plate which was used to fabricate the manway neck was 0.15 per cent carbon, 21.22 per cent chromium, and 11.45 per cent nickel. Examination showed that the cracks ran from the weld seam out into the neck for a distance of ½ to 1 inch, see Fig. 1. The inside surface of the neck also showed a few pits. Upon probing around these areas with a steel point, we found that

the metal was sound and not sugared by intergranular attack, at either the cracks or the pits. The nature of the pits did not suggest corrosion attack and their presence was identified with manufacturing and not with the service conditions. Aside from these imperfections the surface was clean and only slightly tarnished and no signs of general corrosion were visible. This inspection revealed nothing of significance beyond the presence of the cracks, though it was fairly clear that the metal was in a sound ductile condition.

Upon procuring test samples from the sound portion of the neck adjacent to the cracks it was found by simple bend tests that the metal was strong and ductile. Microsections showed the alloy to be quite clean with respect to oxides and other inclusions, though there were some bands of precipitated carbides in the direction of rolling. The grain size suggested that the material had been annealed after rolling at a temperature of about 2000 degrees Fahr. (1095 degrees Cent.). This was later confirmed by heat treatment of separate samples. Carbides at the grain boundaries and a general dispersion of carbides throughout the grains suggested that this alloy may have been heated to or slowly cooled through the carbide precipitation range. Inasmuch as this material is a particularly good example of stainless steel which is susceptible to stress-corrosion cracking we offer a few photographs of the microstructure. Fig. 2 shows the etched structure of the cracked manway neck in the condition as it was received at our laboratory. Fig. 3 shows the structure of a sample after being heated to 2000 degrees Fahr. (1095 degrees Cent.) and quenched in water. In this condition the austenite grain size is similar to the as-received sample. The quenched sample shows some carbide particles segregated in streaks. The austenite grains outside of the carbide streaks are free from precipitated carbide both within the grains and at the grain boundaries. Fig. 4 shows the structure of the quenched sample after being heated to 1000 degrees Fahr. (540 degrees Cent.). This treatment produced a general precipitation of carbides within the austenitic grains and along the grain boundaries, and this effect was increased by heating to 1200 degrees Fahr. (650 degrees Cent.). In each case the samples were heated for two hours at the temperature stated after having been quenched from 2000 degrees Fahr. (1095 degrees Cent.).

A microscopic examination of several of the cracks showed them to be intergranular, closely following the austenite grain boundaries. Alongside the main cracks, or those which were visible to the unaided

eye, there occurred another set on a finer scale which were also intergranular. These are shown in Fig. 5. This is the type usually observed in specimens that have sugared.

Our preliminary examination suggested three possible causes of the failure.

(1) The metal may have been in a poor structural condition with the typical carbide precipitation at the grain boundaries and presumably susceptible to intergranular attack.

(2) The metal may have been in a stressed condition which, in combination with (1), might have resulted in an accelerated attack. The presence of stress was also suggested by the opening up of the cracks upon forming, which process would act to relieve the stresses. The first condition would result in a general uniform surface attack along the grain boundaries and ultimately produce a sugary surface. (We have since observed just such a condition). A stressed condition might very well result in the opening of deep and rapidly forming cracks, the spacing of which would depend on the stress condition.

(3) Brittle failure of ductile metal can occur under conditions of triple tensile stress and a third possible explanation might be the production of such a stress by improper fabricating and operating conditions.

As tests of these ideas we carried out a number of experiments which will be briefly considered in the following. Four specimens of the failed manway neck were boiled in the Strauss solution *(10 per cent H_2SO_4 and 10 per cent $CuSO_4$), after receiving the following heat treatments. The results of our examination are given with the treatments.

(1) As-received. After 21 hours the surfaces were badly sugared. After 138 hours the specimens could be readily broken in the hands.

(2) As-received, heated at 1200 degrees Fahr. (650 degrees Cent.) for 2 hours, and air-cooled. The results were the same as given under (1). (See Fig. 6A).

(3) Water-quenched from 2000 degrees Fahr. (1095 degrees Cent.). After 492 hours there were no signs of sugaring. (See Fig. 6B).

(4) Water-quenched from 2000 degrees Fahr. (1095 degrees Cent.). Heated at 1200 degrees Fahr. (650 degrees Cent.) for two

*59 c.c. of H_2SO_4 (C.P.) (sp. gr. 1.84) and 130 grams $CuSO_4 \cdot 5H_2O$ in water to make 1 liter. Sp. gr. solution at 70 degrees Fahr. = 1.142.

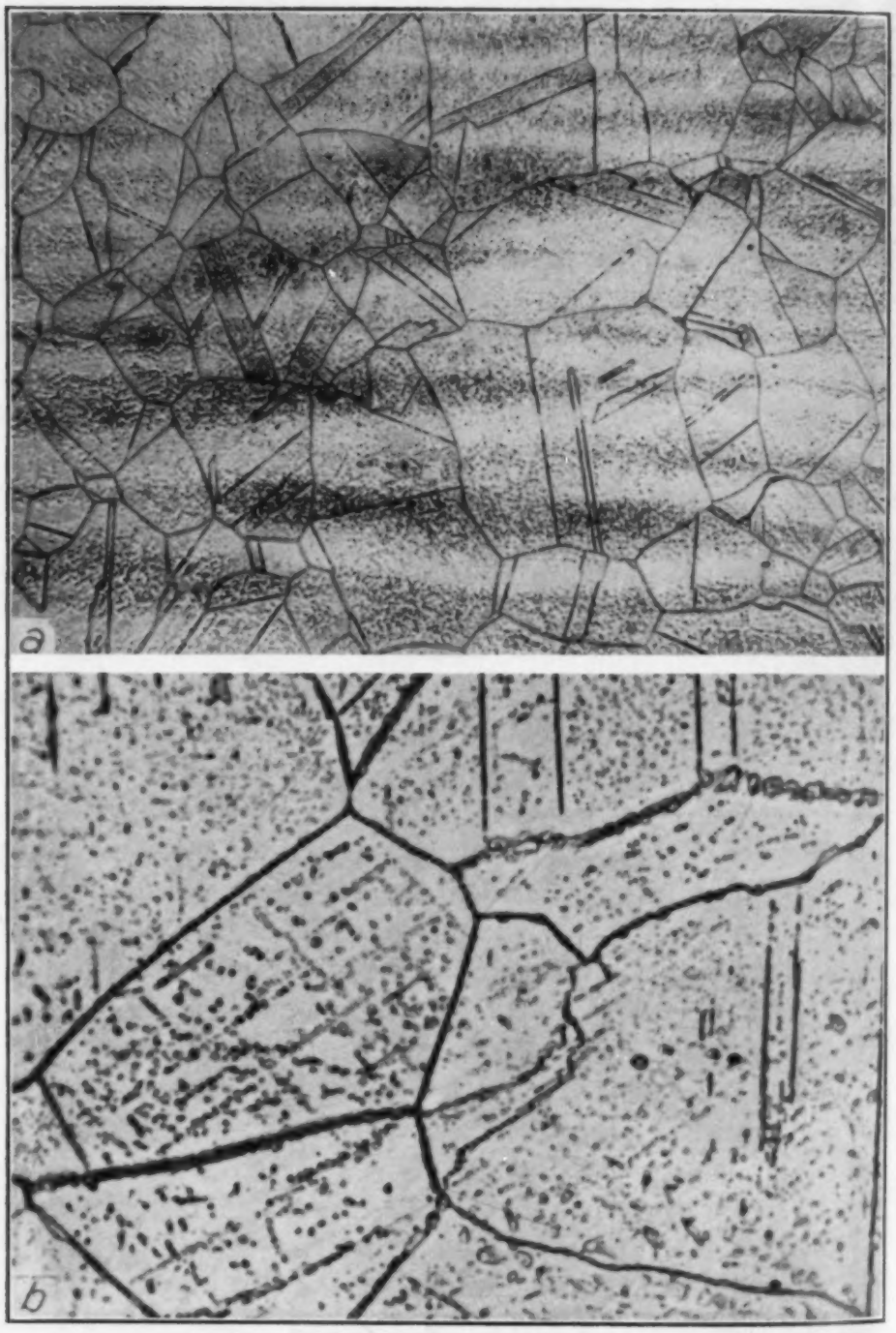


Fig. 2—Type 307 Alloy (21-11). Microstructure of Manway Neck as Received. Electrolytic Etch—10 Per Pent Oxalic Acid.
Fig. 2a—× 100. Fig. 2b—× 2000. Sensitive to Stress-Corrosion Cracking.

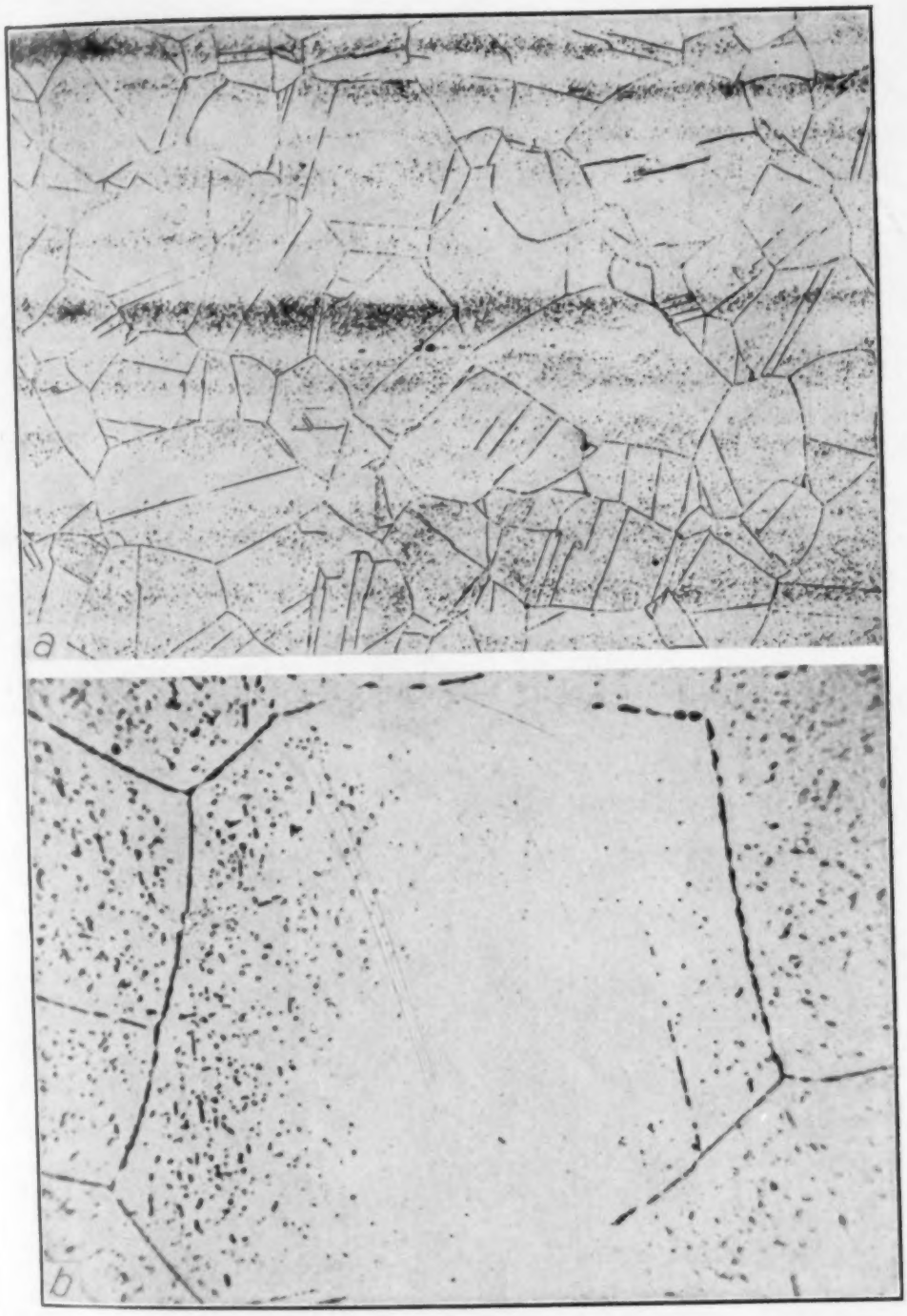


Fig. 3—Type 307 Alloy (21-11). Microstructure of Sample Water-Quenched from 2000 Degrees Fahr. Not Sensitive to S-C Cracking. Electrolytic Etch—10 Per Cent Oxalic Acid.
Fig. 3a—× 100. Fig. 3b—×2000.

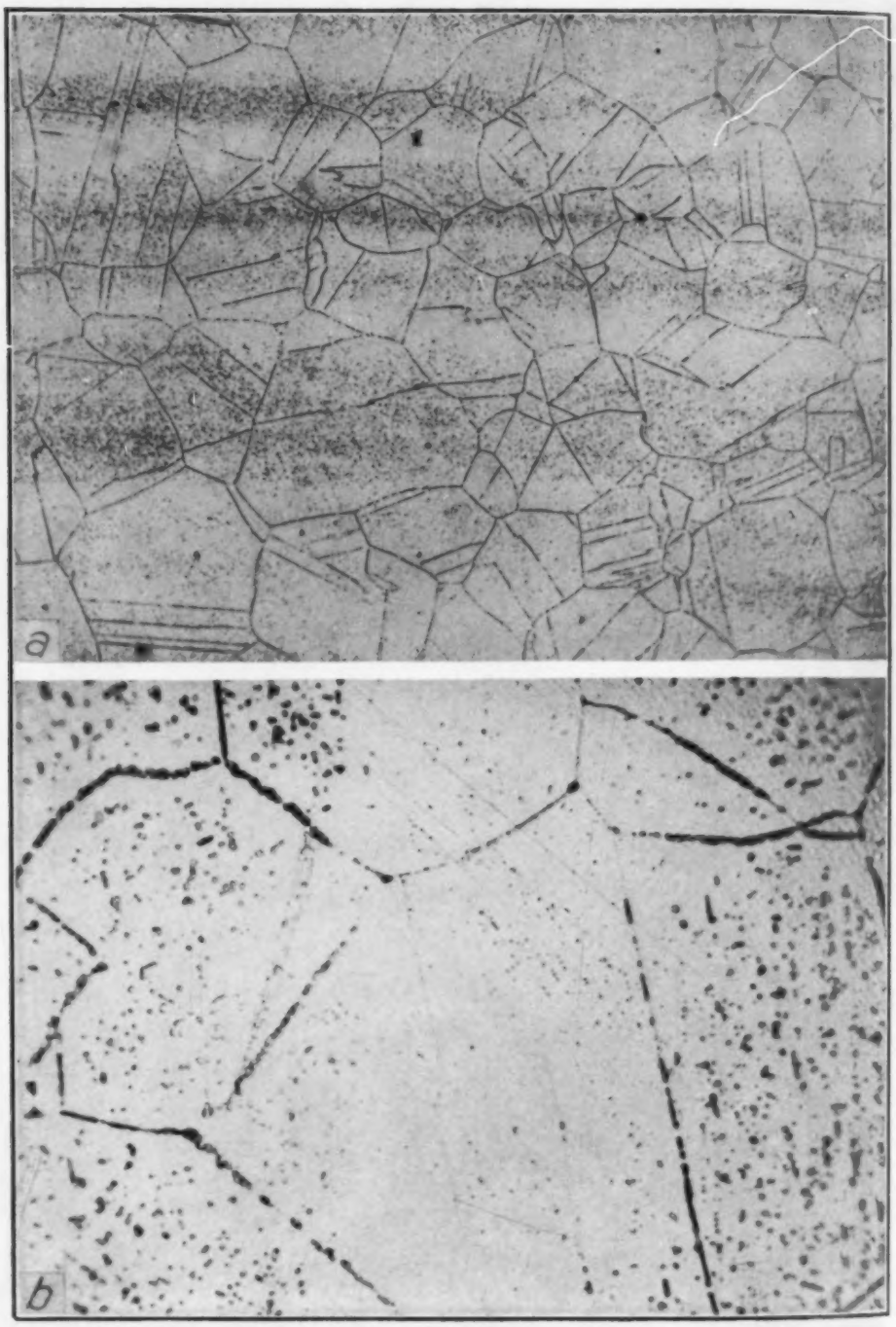


Fig. 4—Type 307 Alloy (21-11). Microstructure of Sample Water-Quenched from 2000 Degrees Fahr. and then Heated to 1000 Degrees Fahr. for 2 Hours. Sensitive to S-C Cracking. Electrolytic Etch—10 Per Cent Oxalic Acid.
Fig. 4a—× 100. Fig. 4b—× 2000.

hours, and air-cooled. After 23 hours the surfaces were sugared. (See Fig. 6C).

In these tests the specimens were periodically removed from the boiling solution and scratched with a steel point to detect any sugaring that might have occurred as soon as intergranular attack had pro-



Fig. 5—Type 307 Alloy (21-11). Microstructure Along Crack in Manway Neck Showing Intergranular Path of Rupture. Electrolytic Etch—10 Per Cent Oxalic Acid. × 100.

gressed around the grains. It was clear that the manway neck was in a very poor structural condition though additional tests were needed to develop the cause of cracking. Figs. 6A, B and C show polished and etched cross sections of the Strauss specimens. These show the banded condition referred to.

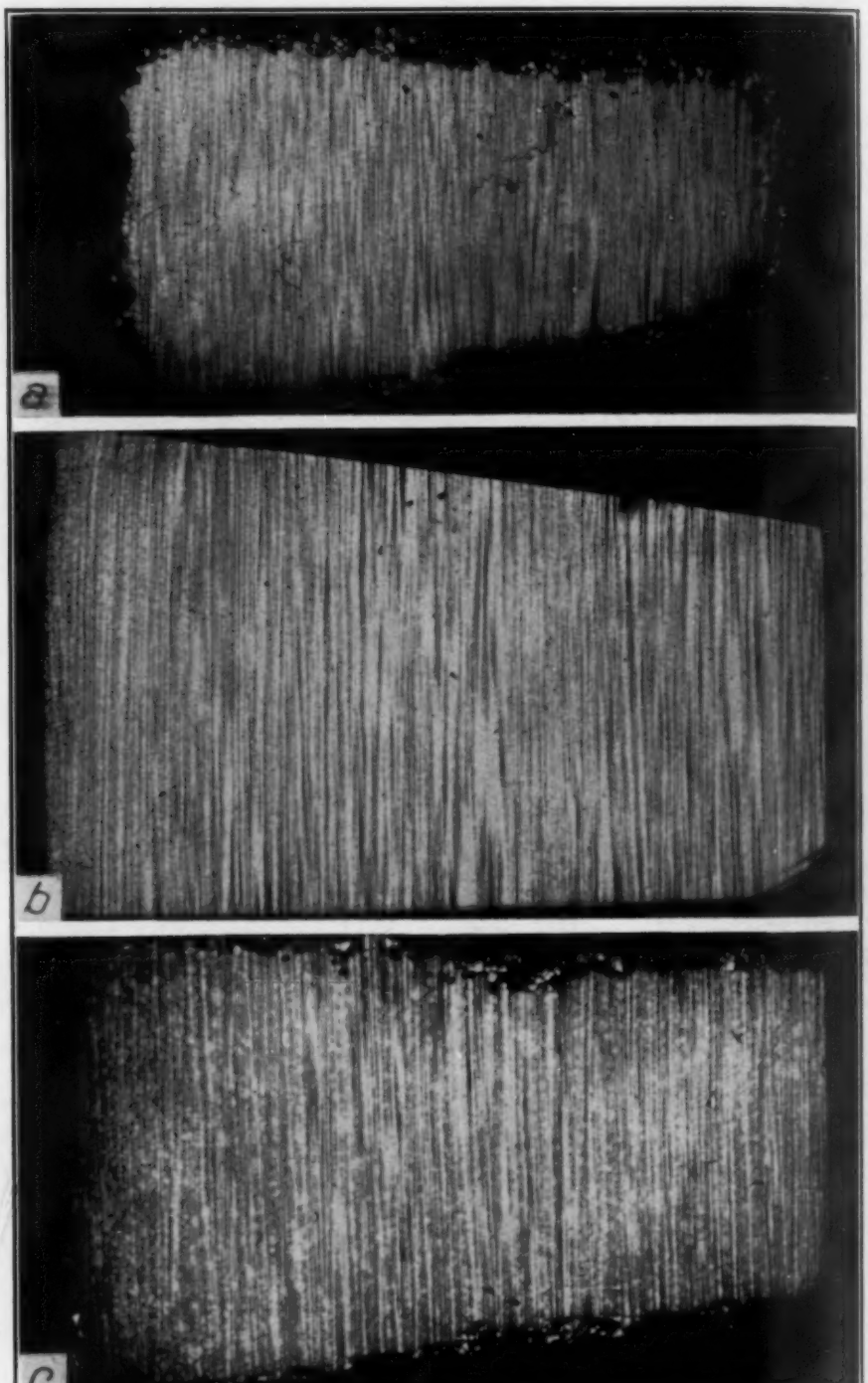


Fig. 6—Type 307 Alloy (21-11). Macrostructure of Manway Neck Samples Tested in Boiling Strauss (Copper Sulphate) Solution. Electrolytic Etch—10 Per Cent Oxalic Acid.

Fig. 6a—Sample as Received and Heated at 1200 Degrees Fahr. for 2 Hours.

Fig. 6b—Sample Water-Quenched from 2000 Degrees Fahr.

Fig. 6c—Sample Water-Quenched from 2000 Degrees Fahr. and then Heated at 1200 Degrees Fahr. for 2 Hours. × 5.

Tests of Stress-Corrosion Cracking

While the tests just described demonstrated that something was wrong with the material of the manway neck, the important elements of stress and strain were lacking. This led us to devise a simple procedure with which to incorporate these factors into corrosion tests. Small strips were cut out of the manway neck which were about 1/8 inch thick by 3/8 inch wide and 3 inches long. These were formed cold around a bar into a horseshoe shape. This operation cold-worked or strained the metal and also put it into a convenient shape for the

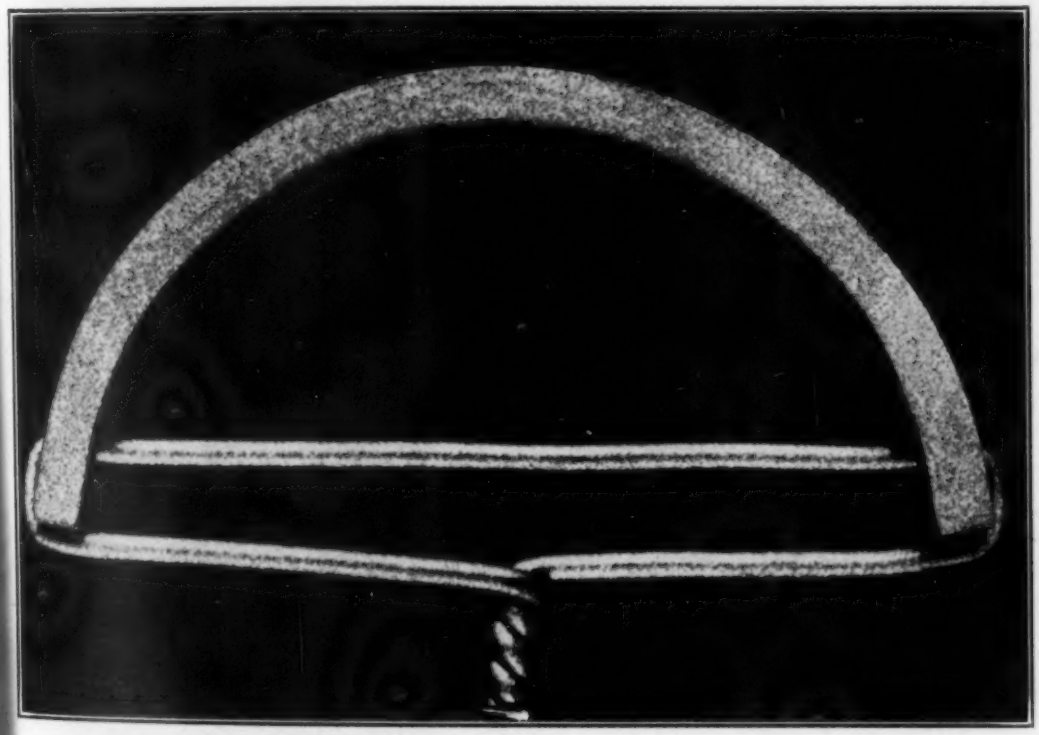


Fig. 7—Horseshoe Sample Used in Tests for Stress-Corrosion Cracking. × 2.

application of an elastic stress by squeezing the ends closer together and holding them elastically sprung with a stainless steel wire. Such a horseshoe sample is shown in Fig. 7. The amount of elastic stress can be varied at will and we shall deal with that aspect of the test later on. These horseshoe test samples are handled in testing the same as though they were the customary straight specimens. The following tests were carried out in the boiling Strauss solution as before.

(1) As-received. After 15 hours the horseshoe specimen cracked on the tension side and showed evidence of sugaring.

(2) The sample was heated to 1950 degrees Fahr. (1065 degrees Cent.) air-cooled, and then deformed cold. After a total time of 1868 hours the specimen was neither cracked nor sugared.

(3) After heating to 1950 degrees Fahr. (1065 degrees Cent.) and cooling in the air, the specimen was deformed cold, heated to 1000 degrees Fahr. (540 degrees Cent.) for two hours, cooled in the air and then elastically stressed. After 24 hours, the specimen was cracked but not sugared. After 48 hours the specimen had begun to sugar.

(4) After heating to 1950 degrees Fahr. and cooling in the air, the specimen was reheated to 1600 degrees Fahr. (870 degrees Cent.) for two hours, cooled in the furnace to 1000 degrees Fahr. (540 degrees Cent.), held for two hours and cooled in the air, and then deformed cold and elastically stressed. After 69 hours, no signs of cracking or sugaring were observed; after 144 hours the specimen showed slight sugaring, and at the end of 1000 hours had completely disintegrated. At no time did this specimen crack open.

(5) The as-received specimen was heated to 1600 degrees Fahr. (870 degrees Cent.) for two hours, cooled in the furnace to 1000 degrees Fahr. (540 degrees Cent.), held for two hours and then air-cooled. It was then deformed cold. After 93 hours there were no signs of sugaring. After 168 hours of total time the surface showed slight sugaring and at the end of 1032 hours it had completely disintegrated. At no time did this specimen crack open.

Typical results of these tests are illustrated in Fig. 8. The top specimen represents the treatment (2) and shows no cracking or sugaring. The center specimen represents the treatment (3) with the crack at the center that developed in 24 hours. The bottom specimen illustrates the complete disintegration of samples treated as in (4) and (5). The microstructure of the sample and the crack of the center specimen of Fig. 8 is shown in Fig. 9. Upon comparing this with the microstructure of the crack in the failed manway neck in Fig. 5 it is obvious that the path of rupture produced in the test specimen is similar to that produced in service—both are intercrystalline.

In the as-received condition the alloy cracked open and sugared in a very short time. A solution heat treatment remedied this condition and neither cracks nor sugaring were found after prolonged boiling in the Strauss solution. After this test we decided to find out if the horseshoe test specimen had been elastically stressed throughout

the experiment. It measured 1.405 inches across the open ends as it came out of the test; after cutting the wire this dimension increased to 1.435 inches which corresponded to an elastic strain of 0.030 inch. When the solution treatment was followed by reheating to 1000 de-

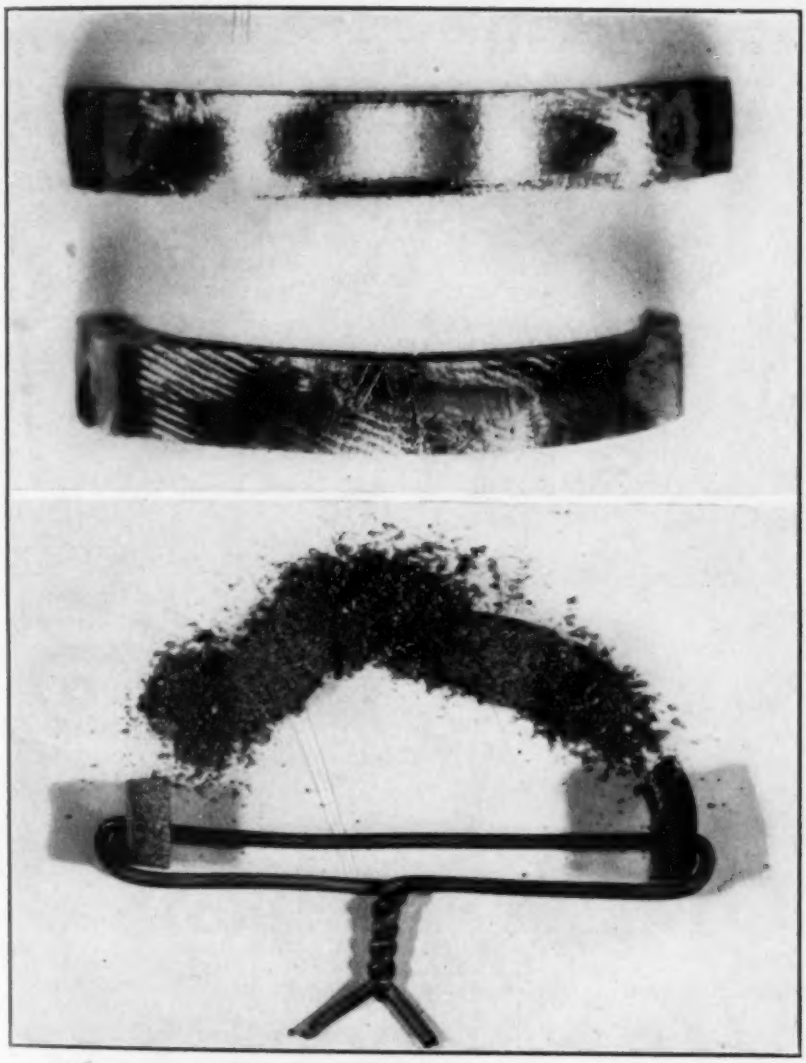


Fig. 8—Type 307 Alloy (21-11). Stress-Corrosion Tests Illustrating (Top) Complete Resistance, (Middle) Stress-Cracking, and (Bottom) Complete Disintegration. × 1.5.

grees Fahr. (540 degrees Cent.) it behaved in the same way as the as-received specimen would and we observed that the crack opened up to relieve the stress before any sugaring occurred. Reheating to a temperature at the upper end of the carbide precipitation range, though followed by a heating to 1000 degrees Fahr. (540 degrees Cent.) produced a decidedly different effect. Two specimens were so treated:

One had previously been given a solution treatment and the other was in the as-received condition. Both reacted similarly and at no time developed cracks though they both sugared badly on prolonged exposure.

These tests seemed capable of yielding positive results on stress-corrosion cracking and we next ran two graded series of tests in each

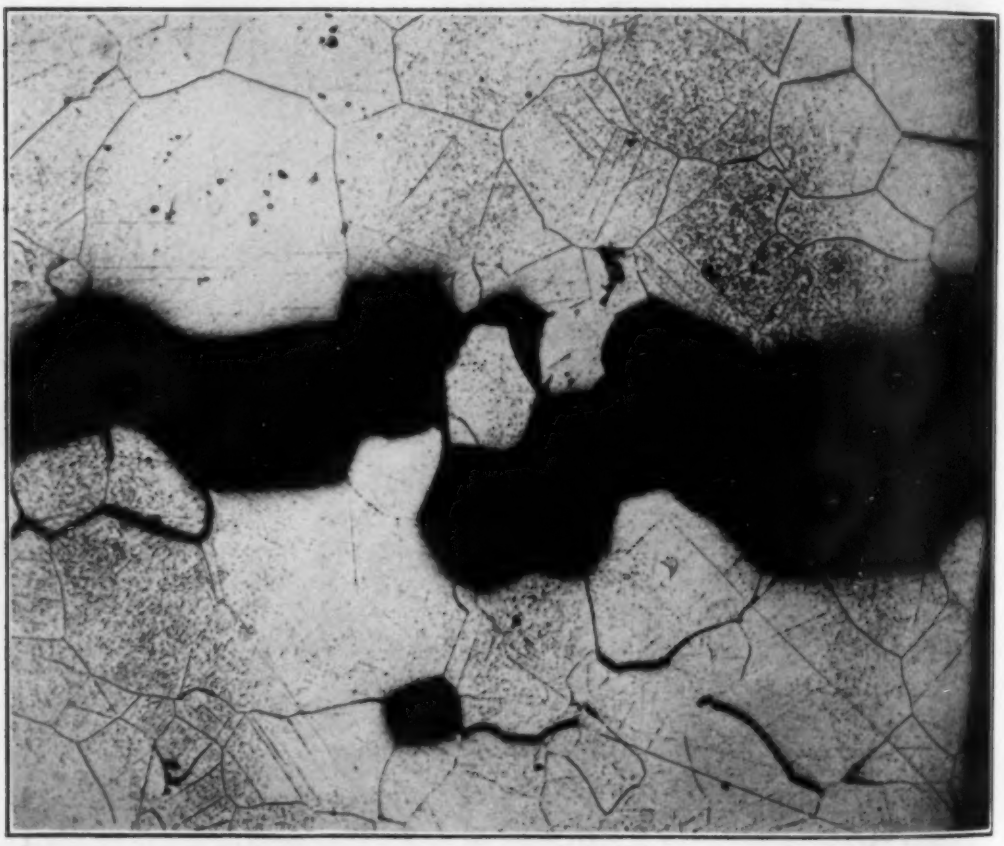


Fig. 9—Type 307 Alloy (21-11). Microstructure at Surface Showing the Appearance of Stress Crack. Electrolytic Etch—10 Per Cent Oxalic Acid. × 100. See Fig. 8.

of which the elastic stress varied from specimen to specimen. The material was taken from the manway neck and the specimens measured 7/64 inch thick by 5/8 inch wide by 3 inches long. This 5/8-inch dimension was the original thickness of the manway. After drilling holes in the ends, each specimen of both series was bent cold into horseshoe shape over a 1¾-inch arbor. Series 1 was run in this condition with different amounts of elastic stress. The specimens of Series 2 were heated to 1850 degrees Fahr. (1010 degrees Cent.), air-cooled, and then reheated to 1200 degrees Fahr. (650 degrees Cent.) for two hours. One specimen of each series was selected to determine the

amount of elastic springing required to produce tensile stresses in the outer fibers of known amounts. This work was done in conjunction with the department of Theoretical Mechanics and Testing of Materials whose results are recorded here. Fig. 10 shows the horseshoe specimen schematically represented. A load P presses the free ends closer together and sets up elastic tensile stresses in the outer fibers whose magnitudes are given approximately by the following formulæ. A more precise calculation is not required for this problem.

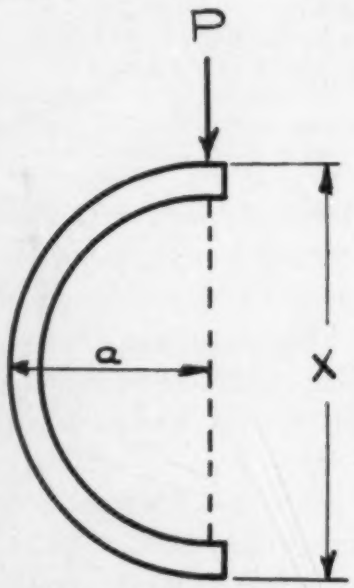


Fig. 10—Schematic Drawing of Horseshoe Specimen.

$$M = Pa$$

$$S = \frac{Mc}{I}$$

in which

P = load
a = lever arm
M = moment on the section
c = ½ thickness
$I = \frac{1}{12} bt^3$
b = width of sample
t = thickness
S = elastic stress

Determinations were made of the loads P and the corresponding deflections, or changes in X, so that with subsequent test samples it was possible to calculate the deflection of X which was required to establish a given elastic stress in the test sample. Results for both series are tabulated in Table I to show the actual outer fiber stresses which were produced in each of the test specimens.

Table I

Series I (No Heat Treatment)			Series II (1850° F. Air Cool + 1200° F. 2 Hr. Air Cool)		
Spec. No.	Compression	Stress p.s.i.	Spec. No.	Compression	Stress p.s.i.
1.	None	None	7.	None	None
2.	0.005″	5,000	8.	0.004″	5,000
3.	0.011″	10,000	9.	0.008″	10,000
4.	0.022″	20,000	10.	0.016″	20,000
5.	0.043″	40,000	11.	0.032″	40,000
6.	0.065″	60,000	12.	0.045″	55,000
	0.096″	87,000 no set		0.047″ {Elastic Limit	58,000
				0.094″	87,000 0.030″ set

The following results were obtained with the first series of specimens. After six hours in the boiling Strauss solution neither cracking nor sugaring was observed. After this treatment the specimens were allowed to remain in the cold solution for 15 days after which no attack was observed. The specimens were then again treated in the boiling solution whereupon cracks began to develop after a total time of nine hours, as follows:

Specimen 1 sugared but did not crack after 9 hours in hot solution. (Not stressed)
Specimen 2 sugared and showed 11 cracks on the stressed bend.
Specimen 3 sugared and showed 11 cracks on the stressed bend.
Specimen 4 sugared and showed 14 cracks on the stressed bend.
Specimen 5 sugared and showed 20 cracks on the stressed bend.
Specimen 6 sugared and showed 21 cracks on the stressed bend.

The specimens of Series 2 showed first signs of failure after 26 hours in the boiling solution. All specimens were sugared but none had cracked. After a total time of 34 hours additional sugaring was noticed but again none had cracked. The same was true after 41 hours but at this period the specimens had sugared so badly that they could be broken in the hands while all the elastic stress had been released.

Additional samples were tested in Aborn's copper sulphate solution* and in the nitric-hydrofluoric acid mixture**. The Aborn solution is adjusted in composition to produce the severest intergranular attack on sensitized metal and does not attack normal metal. The nitric-hydrofluoric acid is probably faster than the copper sulphate solution in its effect but it has the disadvantage of attacking normal metal slowly. Two specimens were deformed cold and stressed elastically about 50,000 pounds per square inch. One was tested in boiling Aborn's solution and one in nitric-hydrofluoric acid at 60 degrees Cent. After 15 hours the former had one large crack, the fractured edges of which were sugared, while the latter specimen was cracked in three places, yet not enough to relieve all the stresses, and was also in a slightly sugared condition.

Two additional specimens were stressed about 35,000 pounds per square inch though with different preliminary treatments. The first one was cold-deformed to horseshoe shape and then elastically stressed. The second one was hot-formed into a horseshoe at about

*13 gr. $CuSO_4 \cdot 5H_2O$ (C.P.) and 47 c.c. H_2SO_4 (C.P.) (1.84 sp. gr.) per liter (approximately 1 per cent $CuSO_4$). This solution is employed boiling.

**20 per cent HNO_3 (C.P.) (1.42 sp. gr.) by volume and 4 per cent HF (48 per cent) (C.P).

1700 degrees Fahr. (925 degrees Cent.), then heated to 1850 degrees Fahr. (1010 degrees Cent.) and air-cooled, and then heated to 1000 degrees Fahr. (540 degrees Cent.) for two hours. After cleaning the surface, the second sample was elastically stressed and both specimens were placed in Aborn's solution. After 1½ hours the first specimen had cracked and was found to be sugared locally on the outer bend. After 31 hours the second specimen was not cracked or sugared. At this time it was removed from the solution and deformed plastically by closing the ends of the horseshoe to produce a permanent set of 0.010 inch as measured across the open ends. This raised the yield point to about 85,000 pounds per square inch. After this treatment the specimen was stressed elastically as before to about 35,000 pounds per square inch and again placed in the boiling Aborn solution. After 40 hours this specimen developed a large crack which relieved the stress and was also sugared. It appears from this that this alloy must be work hardened to make it susceptible to stress cracking. We do not know the amount of cold working that is required but it is of interest to note that a re-examination of microsections from the failed manway neck showed just that condition at the surface. Fig. 11 represents a cross section through the manway neck and shows strain markings very close to the inside surface of the neck adjacent to the open cracks. A solid nozzle of 23-11 alloy in this manway neck had also failed by cracking and our examination of it revealed similar strain markings. This nozzle was made by drilling out a solid bar. The carbides in this nozzle were in about the same condition as has been described for the neck proper.

The work which had been done up to this point showed that strain or cold working as well as elastic stress was necessary to produce stress-corrosion cracks in this alloy when it was in a susceptible structural condition. Our test with different elastic stresses did not suggest that a critical stress was required to produce stress cracking. All of this work had been done on one steel and we next subjected samples of various commercial steels to tests for susceptibility to stress-corrosion cracking.

Tests of Commercial Stainless Steel

After this preliminary investigation many hundreds of tests were run on commercial steels, representing eight different types of stainless steels, from five different producers. All specimens were

cold-deformed in the as-received condition which in almost all cases meant the annealed condition, free from intergranular susceptibility. After drilling the hole at the ends and forming to the horseshoe shape each set of steels in this program was given 27 different heat

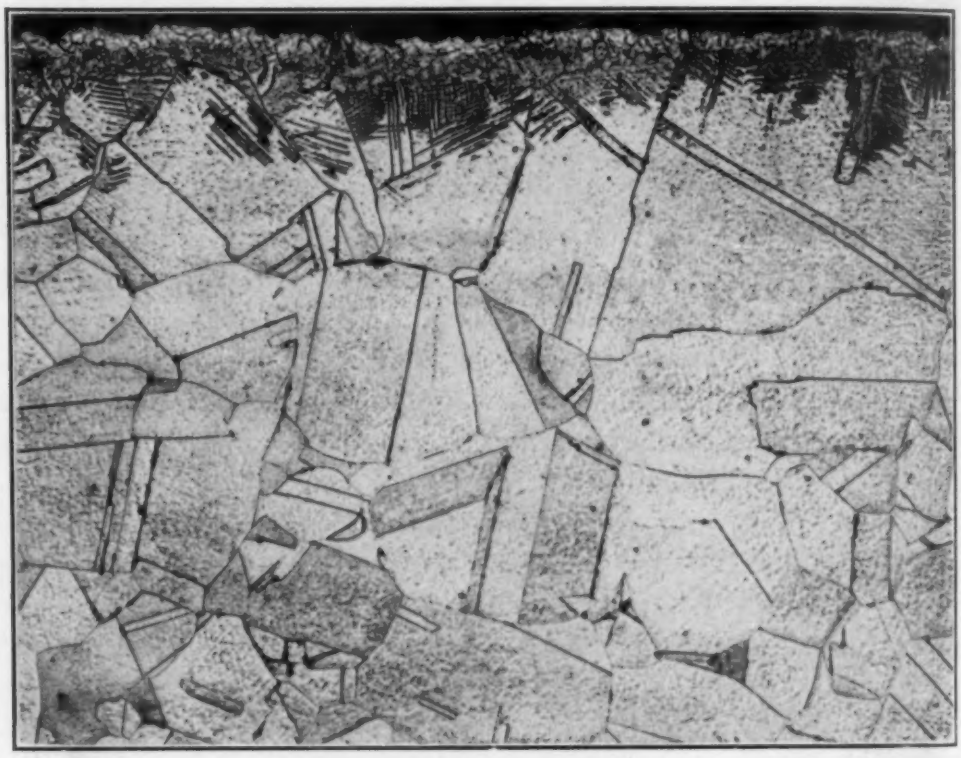


Fig. 11—Type 307 Alloy (21-11). Microstructure at Surface Showing Strain Markings on Inside Surface of Manway Neck Adjacent to Open Cracks. Electrolytic Etch—10 Per Cent Oxalic Acid. × 100.

treatments which were devised to introduce the following factors into the tests: Carbide precipitation for various times and at various temperatures: re-solution and re-precipitation of carbides: coarsening of the austenite grain size; and desensitization within the carbide precipitation range. All the specimens were stressed as uniformly as possible, depending upon the yield point of the material, to not less than 35,000 pounds per square inch and not over 55,000 pounds per square inch and placed in the nitric-hydrofluoric acid mixture at 60 degrees Cent. Our reason for selecting this solution was the rapidity with which it develops stress cracking in sensitive metal. After several hundred specimens had been tested we found only a few that failed by stress cracking though the samples had been cold-formed prior to heat treatment. The results are shown in the following tabulation.

Table II

Analysis	Type	No. of Heats	No. of Failures by Stress Cracking
19-9 S + Ti	321	3	None
19-10S + Cb	348	5	None
18-8 S	304	1	None
18-8 S + 3 Mo	316 + 317	8	2 Heats
20-10S	308	1	None
21-11	309	1	1 Heat
25-20S	310	1	None
25-18S + Cb	310 Cb	1	None
25-13S + Cb	309 Cb	1	None

Many of these samples which were heated within the carbide precipitation range showed preferential corrosion on the stressed bend, but few showed actual cracking. The samples of type 304 (18-8) sugared after 22 of the heat treatments used but in no case gave evidence of stress cracking. Many of these specimens had been severely corroded but, after test, were still in a stressed condition. Two heats of the type 316 alloy, (18-8 + Mo) showed three failures by stress cracking. Of two samples from one heat, both of which had been heated to 1950 degrees Fahr. (1065 degrees Cent.) and air-cooled, one had been heated for two hours at 1200 degrees Fahr. (650 degrees Cent.) and the other for 15 minutes at 1300 degrees Fahr. (705 degrees Cent.). The sample which had been heated to 1200 degrees Fahr. (650 degrees Cent.) cracked in 200 hours, and at this time the specimen was sugared. The microstructure at the surface of this specimen, showing sugaring, is given in Fig. 12a. The specimen which had been heated to 1300 degrees Fahr. (705 degrees Cent.) cracked after 400 hours and had also sugared. The third sample was from another heat and had been cold-deformed as-received and then heated to 1200 degrees Fahr. (650 degrees Cent.) for two hours. Open cracks and sugaring were noted after 24 hours immersion. The appearance of this crack running from the surface into the sample is shown in Fig. 12b. A marked difference in grain size of these two samples is apparent. The compositions of these two heats are:

C	Cr	Ni	Mo	
0.07	18.8	11.2	3.0	This heat produced two failures
0.08	18.0	10.7	2.5	This heat produced one failure.

The time of the test varied with the sample but when the occasion warranted we did not hesitate to use periods up to several thousand hours though this is usually regarded as being an excessively drastic treatment. This solution does attack normal metal very slowly though we have held samples in the hot solution over 3200

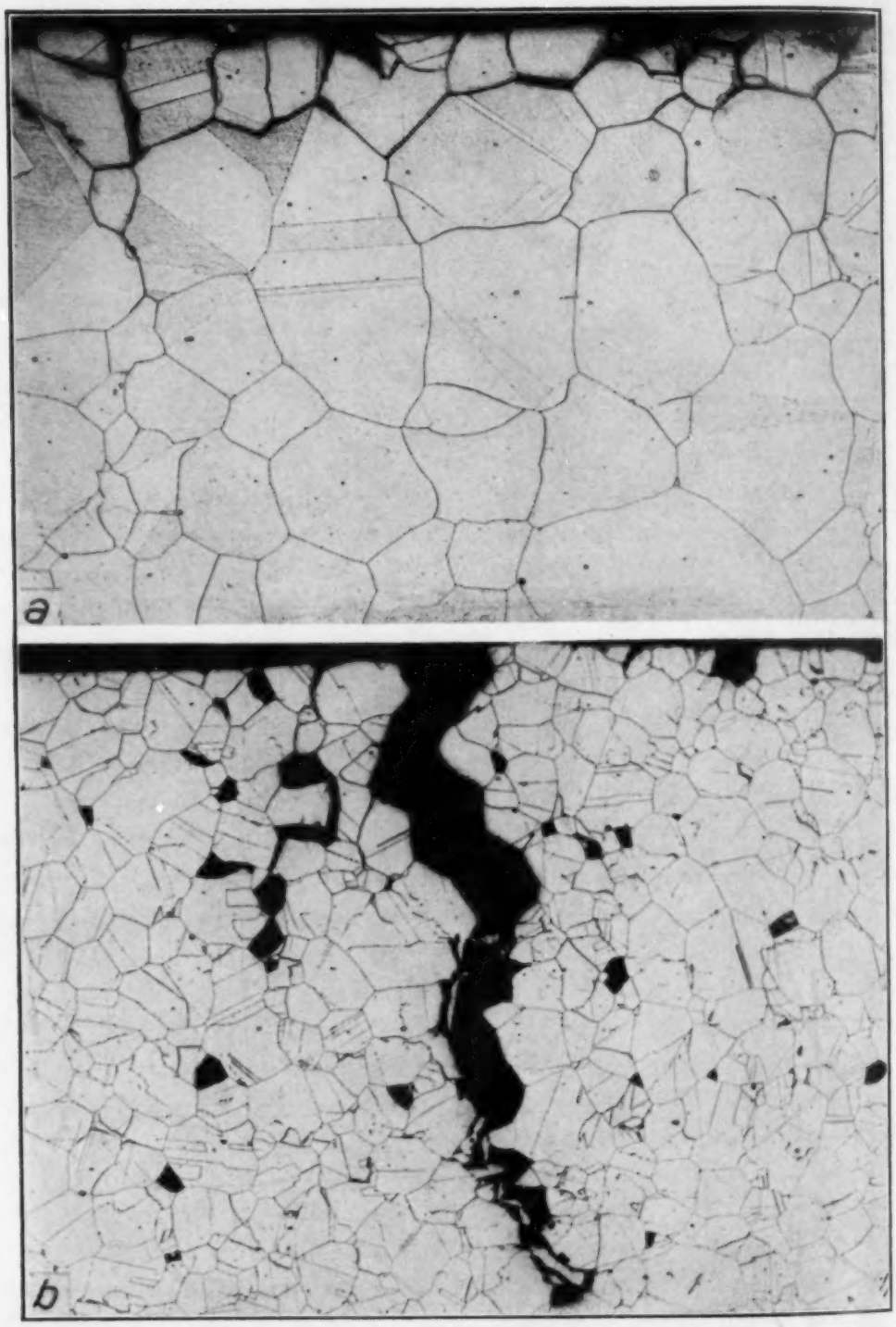


Fig. 12a—Type 316 Alloy (19-11 SMo). Microstructure at Surface Showing Sugaring. Electrolytic Etch—10 Per Cent Oxalic Acid. × 100.
Fig. 12b—Type 316 Alloy (18-11 SMo). Microstructure at Surface Showing Appearance of Stress Crack. × 100.

hours without severe attack. In all cases the acid was changed about every 48 hours. During this time several sets of pyrex glass beakers were corroded so that we are convinced that an active amount of hydrofluoric acid remained in the solution at 60 degrees Cent. Most of our specimens were tested for about 1000 hours, a few were held 2000 hours, and all of the as-received and cold-deformed samples were held for 3000 hours.

Without attempting to record all the data, we can summarize these findings on stress-corrosion cracking as follows:

(1) No specimen that cracked was free from carbide precipitation and intergranular attack.

(2) On the other hand stainless steels, with or without stabilizers, were attacked intergranularly (sugared) with no signs of stress cracking.

(3) The variations of the austenite grain size and in the chemical composition which were included in the test could not be correlated with stress-cracking though this is necessarily limited to type 316 steel.

(4) Alloys which were in a good structural condition were not susceptible to stress-cracking. From these tests and others of a similar nature it appears that these steels have to be put in a sensitized condition though apparently certain heats are more susceptible to stress-cracking than others.

Tests Under Service Conditions

Our laboratory has made a definite effort to test out the susceptibility of various commercial steels under conditions which are as nearly as possible representative of the service condition. We also test duplicate sets of stress-corrosion specimens in the laboratory under accelerated conditions. In many cases we have duplicated failures which occurred under operating conditions. Our horseshoe sample lends itself admirably to this type of testing and can be used whenever the prospective user can supply equipment in which the test samples can be placed. Under these circumstances, even though we know nothing about the service conditions themselves, a reasonably safe guide can be secured for the selection of the steel and the fabrication procedure. Stress-corrosion tests of this type have been part of our routine customer's service tests for the

past two years, during which time we have radically reduced the number of test specimens which are needed to represent each type of steel. It is the purpose of these specimens to bring to our attention the characteristics of the customer's corrosion conditions and to accomplish this we may vary the treatments to produce both good and poor structures in the particular alloy. If stress and strain affect the corrosive attack, or produce stress-corrosion cracking, that is brought out. The samples are also weighed before and after the test so that the effects of general corrosion can be properly evaluated. We are giving herewith a summary of our findings in one such test.

Five stainless alloys were selected for this test, three of which were recommended for the service conditions and two of which were added to complete the survey. The heat treatments were designed to take care of various methods of fabrication, which included solid stainless construction, layer construction, and lined construction. These three methods of fabrication do not necessarily involve the same set of heat and mechanical treatments and we found it necessary to make up eleven specimens of each steel to include all of the important variables. Ten of these specimens were made with arc deposited beads of suitable weldrod analysis. Many of the specimens were deformed hot and some were deformed cold while heat treatments were performed before and after bending to horseshoe shape. Before applying the wires, all surfaces were cleaned by a standard procedure to remove scale, weld sputter, and any iron particles which might be on the surface. Before wiring, each specimen was weighed to ± 0.001 grams and the surface area was calculated. The wire used to stress the horseshoe was put in the best possible condition to resist attack and was weighed separately so that if it should be attacked during the test, accurate data for the test specimen proper could still be obtained. However, for routine weighing during the course of a test, the wired specimens are always weighed as a unit. Our preliminary studies showed that the actual amount of stress in the horseshoe is not particularly critical. On this account a sufficiently uniform stress condition of high enough intensity to produce cracking in susceptible material can be produced by using a gage across the open ends of the horseshoe. Our practice is to bend up a 3-inch long specimen around a 1¾-inch bar springing the ends about 0.03 inch, depending on the cross section to an elastic stress of not less than 30,000 pounds per square inch. The specimens were placed in a woven alloy wire basket which had previously been heat treated

to insure the best corrosion resistance. This basket of samples was then placed in a pilot plant unit which subjected all the samples to the correct temperature, pressure, etc. Details of these test samples and the heat analysis are given in Table III.

Table III

Plate Composition

Steel Number	Type Number	C	Mn	Si	Cr	Ni	Mo	Cb	
1	316	0.08	1.38	0.35	18.0	10.7	2.5	...	18-10 + Mo
2	304	0.05	0.45	0.28	19.2	9.0	...	...	19-9
3	309 Cb	0.12	1.21	...	25.5	13.6	...	0.90	25-13 + Cb
4	317 Cb	0.07	1.31	0.62	18.1	8.6	3.0	1.06	18-8 + Mo + Cb
5	348	0.08	..	0.41	20.0	9.0	...	0.82	20-9 + Cb

Weld Composition

Steel Plate	Weld Metal	C	Mn	Si	Cr	Ni	Mo	Cb	
1	18-8 + Mo	...	...	...	...	...	...	...	
2	22-12	0.05	0.72	0.5	19.0	12.2	...	...	Deposit
3	25-12 + Cb	0.11	0.62	0.58	22.7	13.7	0.03	1.14	Deposit
4	18-8 + Mo + Cb	0.07	1.64	...	19.4	10.3	2.5	0.71	Rod
5	18-8 + Cb	0.06	0.65	...	18.9	9.5	...	0.74	Rod

The arc weld deposits were made with coated rods directly on the alloy sheets. The sheets were clamped against a chill plate and a heavy bead of weld metal was deposited which penetrated about ⅔ the thickness of the stock. These arc weld deposits gave us samples of actual weld metal for test purposes and also produced a heat effect which could be used to determine the sensitivity of a plate material. After laying down this weld bead, the samples were treated as follows:

1. As-Received—Not welded—deformed cold to horseshoe—sandblasted, then stressed.
2. Arc Welded—Deformed hot—then heated 2100 degrees Fahr. (1150 degrees Cent.)—¼ hour—Air Cool.
3. Arc Welded—Deformed hot—then heated 1600 degrees Fahr. (870 degrees Cent.)—2 hours—Air Cool.
4. Arc Welded—Deformed hot—then heated 1600 degrees Fahr. (870 degrees Cent.)—2 hours—Air Cool + 1200 degrees Fahr. (650 degrees Cent.)—four hours—Furnace Cool.
5. Arc Welded—Deformed hot—then heated 2100 degrees Fahr. (1150 degrees Cent.)—¼ hour—Air Cool + 1600 degrees Fahr. (870 degrees Cent.)—2 hours—Air Cool + 1200 degrees Fahr. (650 degrees Cent.)—4 hours—Air Cool.
6. Arc Welded—Deformed hot—then heated 1200 degrees Fahr. (650 degrees Cent.)—4 hours—Furnace Cool.
7. Arc Welded—Deformed hot—then heated 1000 degrees Fahr. (540 degrees Cent.)—4 hours—Furnace Cool.
8. Arc Welded—Deformed cold—No further treatments.
9. As-Received Plate. Heated to 1200 degrees Fahr. (650 degrees Cent.)—4 hours—Furnace Cool—then arc weld—deform cold.
10. As-Received Plate. Heated to 1600 degrees Fahr. (870 degrees Cent.)—2 hours —Air Cool + 1200 degrees Fahr. (650 degrees Cent.)—4 hours—Furnace Cool—then arc weld—deform cold.

11. As-Received Plate. Heated to 1600 degrees Fahr. (870 degrees Cent.) —2 hours—Air Cool—then arc weld—deform cold.

Some results of these service tests are recorded below, by number.

Steel No. 1—Type 316, 18-11 + 2.5 Mo

(4) Failed in stock after 105 hours with no previous indications of cracking.
(5) Failed in stock after 49 hours—Evidence of attack appeared after 30 hours exposure.
(6) Failed at the edge of weld after 15 hours.
(7) Failed in the stock after 128 hours.
(9) Failed in the stock after 15 hours.
(10) Failed in the stock after 15 hours.
(11) Failed in the stock after 174 hours.

The above specimens appear intergranularly attacked on the rough, cracked surfaces after being opened for inspection. There were no signs of sugaring on the original outside surfaces or on the weld metal. On a similar series of stress-corrosion specimens, some of which were tested in the laboratory in boiling copper sulphate solution, we observed that a treatment similar to (9) produced cracking and sugaring in 24 hours' time. The specimen with treatment (5) which failed in the stock after 49 hours, was found to be sugary on the surface of the crack. As a further test the opposite leg of the horseshoe was bent cold in a vise. The maximum bending occurred at a stamped identification number, yet after bending 180 degrees no signs of cracking were observed on the outside surface. This test demonstrated that the metal remained in a ductile condition even after stress-corrosion cracking had occurred. Experience with the specimen (9) was different. Failure in the stock of (9) was reported after 15 hours. We found on examination in the laboratory that two fine cracks came adjacent to the main crack and that the metal in the vicinity was sugary. On bending the opposite leg of the horseshoe, which appeared to be perfectly sound, several cracks opened up on the surface after bending 90 degrees.

Steel No. 2—Type 304, 19-9

(6) Failed at edge of weld after 49 hours. Evidence of attack appeared after 30 hours exposure.
(9) Failed in the stock after 15 hours.
(10) Failed in the stock after 82 hours. Evidence of attack appeared after 30 hours.

The above specimens appear intergranularly attacked.

Steel No. 3—Type 309 Cb, 25-13 + Cb

This steel appeared brittle in bending hot or cold and a few of the specimens were cracked in preparation. No specimens showed stress-cracking after 650 hours.

(2) Originally cracked through stamped identification number when deforming at about 1950 degrees Fahr. (1065 degrees Cent.).

(6) Thought to be originally cracked during forming and reported with small crack after 128 hours.

Steel No. 4—Type 317 Cb, 18-8 + 3 Mo + Cb

This steel had a tendency to crack when deformed at moderate temperatures. No specimens showed stress-cracking after 650 hours.

(4) Originally cracked next to the weld deforming at 1600 degrees Fahr. (870 degrees Cent.).

(6) Originally cracked next to the weld deforming at 1200 degrees Fahr. (650 degrees Cent.).

Steel No. 5—Type 348, 20-9 + Cb.

Samples of this steel have shown no failure after 650 hours.

It is obvious that the test conditions in the customer's plant produce stress-corrosion cracking in susceptible metal. The advantage of using a stabilized austenitic stainless steel for resisting corrosion of certain types is also obvious. It may be of interest to note here that we have observed stress-corrosion cracking in another customer's test though the conditions there were of the type that produce general corrosion rather than intergranular attack.

These test results showed, what appears to be generally true in our experience, that there is no particular unstabilized austenitic type of stainless steel that does not become susceptible to stress-corrosion cracking when put into a "bad" structural condition. This seems to hold though the nickel and chromium contents be increased and though the carbon content be held on the low side. It seems preferable to use stabilized alloys for service of this type or else to utilize a heat treatment after fabrication which is capable of eliminating susceptibility of stress-corrosion cracking.

Closure

What causes stress-corrosion cracking? The answer to this question is not fully understood and hundreds of tests that we have made do not bring forth a simple explanation of the phenomena.

The first prerequisite concerns the nature of the corrosive medium or at least it has been our experience that those media that tend to attack stainless steel intergranularly appear to be most effective in producing cracking. The second requirement, and here we can be somewhat more positive, appears to be that the metal must be susceptible to intergranular attack when under certain conditions of stress and strain. This statement requires elucidation. Reverting to Steel No. 1, seven of eleven samples of which failed under our customer's operating conditions, our heat treatment (7) which is 1000 degrees Fahr. (540 degrees Cent.) for four hours, produced stress cracking in 128 hours. Comparing this with the behavior when not stressed and strained is of interest. In laboratory tests on flat specimens which were neither stressed nor strained, samples of this same steel were heated to 1100 degrees Fahr. (595 degrees Cent.) for two hours. After 1250 hours in the boiling Strauss solution no signs of sugaring were observed. A second sample heated to 1000 degrees Fahr. (540 degrees Cent.) for two hours was boiled for 1600 hours in the same solution without sugaring. (It will be recalled that 1200 degrees Fahr. (650 degrees Cent.) for four hours caused this steel to sugar). Horseshoe specimens which have failed under operating conditions have been found to be ductile on both sides of the failure, showing that the metal had not been intergranularly attacked generally. On the other hand we have always observed intergranular attack along the main path of rupture in stress-corrosion test samples. This suggests that stress itself is an accelerator of corrosion and this appears to be confirmed by horseshoe samples which have shown preferential or early sugaring on the tension face of the horseshoe sample. While it is pointed out here that susceptibility to intergranular attack is a necessary prerequisite for stress-corrosion cracking we do not find that a condition of the metal which produces sugaring always produces cracking when stressed and strained. Certain heats of steel when in a sensitive condition appear to be more susceptible to stress-corrosion cracking than others. Our efforts so far to analyze this behavior have not been entirely satisfactory. Composition may be a factor but we have not definitely proved it to be so. Austenitic grain size does not correlate with stress-cracking in the observations we have made, though this is limited to the Type 316 steels (18-8 + Mo). Another variable behavior which we have found with the 18-8 + Mo steels is that some do and others do not become desensi-

tized by heat treatment. Some data on this point may be recorded here. A metal which was not sensitive to stress-corrosion cracking was found not to sugar in the boiling Strauss solution in 1200 hours after the following heat treatments.

C 0.07%, Mn 0.37%, Si 0.30%, Cr 18.1%, Ni 9.4%, Mo 3.2%.

1500 degrees Fahr. (815 degrees Cent.) for 15 hours.
1500 degrees Fahr. (815 degrees Cent.) for 30 hours.
1400 degrees Fahr. (760 degrees Cent.) for 15 hours.
1400 degrees Fahr. (760 degrees Cent.) for 30 hours.
1300 degrees Fahr. (705 degrees Cent.) for 15 hours.
1300 degrees Fahr. (705 degrees Cent.) for 30 hours.

A second sample from another heat of the Type 316 steel which did crack in stress-corrosion tests gave the following results.

C 0.05%, Mn 1.40%, Si 0.18%, Cr 18.3%, Ni 10.7%, Mo 2.8%.

After 1500 degrees Fahr. (815 degrees Cent.) for 15 hours; sugared after 734 hours in the Strauss test.

After 1500 degrees Fahr. (815 degrees Cent.) for 30 hours; O.K. after 1100 hours in the Strauss test.

After 1400 degrees Fahr. (760 degrees Cent.) for 15 hours; sugared.

After 1400 degrees Fahr. (760 degrees Cent.) for 30 hours; sugared.

After 1300 degrees Fahr. (705 degrees Cent.) for 15 hours; sugared.

After 1300 degrees Fahr. (705 degrees Cent.) for 30 hours; sugared.

It appears that the molybdenum in the first steel cited was acting as a stabilizer. The second steel of Type 316 after being given our heat treatment (11) sugared in the Strauss solution after 547 hours. In the service test a similarly treated specimen in the form of a stress-corrosion specimen failed by cracking after 174 hours.

To date we have not found stress cracking with the stabilized alloys (columbium and titanium treated steels). Many of these have sugared or have shown general corrosive attack but none actually cracked open. Properly quenched austenitic stainless steels were also not found to crack from stress-corrosion attack.

In closing we wish to express our appreciation to the officials of the A. O. Smith Corporation for permission to publish the results of this study, and to Mr. E. Montania for his valuable assistance in the preparation of the specimens and photomicrographs.

DISCUSSION

Written Discussion: By K. E. Luger, metallurgical engineer, Stainless Steel Division, Carnegie-Illinois Steel Corp., Houston, Texas.

The authors are to be congratulated for presenting a very valuable contribution to stainless steel literature. The users, fabricators, and producers of stainless steel should all be indebted for the large amount of experimental work done and for the excellent manner in which it is presented.

The authors have clearly shown that stress-corrosion cracking very likely cannot occur in austenitic stainless steels unless four conditions are present: (1) the material must be in at least a slightly work hardened condition, (2) it must be under stress, (3) its structural condition must be such as to make it susceptible to intergranular corrosion, and finally, (4) it must be exposed to a corrosive condition that will develop intergranular attack. If any one of these four conditions is absent, stress-corrosion cracking very likely will not occur. Susceptibility to intergranular attack can be eliminated by use of a stabilizing addition to the alloy or by heat treatment, while the work hardened condition can, of course, be eliminated by an annealing treatment. The authors have made a particularly valuable contribution by so clearly proving the importance of the work hardened condition of the material.

There is no doubt but that the methods of testing and the shape of the test pieces developed by the authors will prove to be of great benefit in the future in the determination of which of the austenitic stainless alloys may be suitable for a given service, and how the material should be fabricated (including possible heat treatment by the fabricator) to best withstand the intended service.

If the authors would feel free to present additional information on the following points, it is believed that the paper would be of even greater value:

(1) Were the two heats of Type 316 alloy mentioned on page 209 the only heats of the lot tested which showed cracking? If they were not, any detailed information as to the chemistry and the heat treatment of the other specimens that failed would be of interest.

(2) Do the authors have available photomicrographs of higher magnifications of the structures shown in Figs. 12A and 12B?

(3) Detailed analyses of the two heats of Type 316 steel mentioned on page 217 again would be helpful.

The findings and conclusions of the authors agree very well with the writer's experience. It is highly gratifying to have the authors put to an end for once and all the theory somewhat prevalent several years ago that high alloy content (percentage of chromium plus the percentage of nickel) of austenitic stainless steels was of more importance than maintaining low carbon content. The experiences described with the alloy containing 0.15 per cent carbon, 21.22 per cent chromium and 11.45 per cent nickel both in service and in the authors' extended tests were what might be expected on an alloy having no stabilizing agent and with this relatively high percentage of carbon.

It is believed that the cracking reported on the two heats of Type 316 alloy mentioned on page 209 should not be considered a condemnation of this material, inasmuch as the harmful heat treatments were quite drastic and be-

cause the alloy at its best is not considered to be particularly adapted for resisting hot nitric acid, which was used in the nitric-hydrofluoric acid corroding agent.

As a check on the susceptibility of the austenitic chromium-nickel steels to intergranular corrosion after various heat treatments, the writer believes that electrical resistivity measurements before and after exposing the specimens to the corroding media might prove to be a much more sensitive test than attempting to detect intergranular corrosion by evidence of sugaring of the specimens. This might prove to be particularly of value when submitting specimens for tests under actual operating conditions. These electrical resistivity measurements are fairly easy to make and they will show up intergranular attack even if this is present only to a slight degree.

It is unfortunate that the low carbon 18-8 titanium alloy Type 321 was not included in the test conducted on materials covered in Table III.

It is very interesting to note that the test conducted on materials given in Table III with various heat treatments apparently indicated that none of the materials in the "As-welded not subsequently heat treated" condition (Treatment No. 8) showed evidence of failure. Because of this it would appear that heat treatment following welding is not always essential, even on alloys without stabilizing agents, provided, of course, that the alloys contain relatively low carbon.

The reported fracture in hot and cold working of Steel No. 3—Type 309 Cb —can perhaps be explained by the relatively high chromium and columbium content, together with the relatively low nickel and manganese contents; that is, the material likely had present in its structure copious amounts of high temperature ferrite.

We have, on a number of occasions, experienced cases of stress corrosion on properly heat treated 18-8 alloys where the corroding media have contained halides. It is possible that in these cases and in those presented by the authors, that the cracking is due to the same thing, namely, stress concentration at notches produced in one case by halide pits and in the other by intergranular corrosion.

The effectiveness of such tests as were carried out in the nitric-hydrofluoric acid solution might have been greater if the solution had been changed at frequent intervals rather than every 48 hours. The solution undoubtedly changed to some extent with this long an exposure to glass and metal thus affecting to some extent the results.

Written Discussion: By R. H. Aborn, research laboratory, U. S. Steel Corp., Kearny, N. J.

The phenomenon discussed by the authors of this paper is of unusual interest to us as it appears to be intergranular corrosion aggravated by cold work. Several years ago we observed that an austenitic stainless steel specimen subjected to cold work and then exposed to a favorable sensitizing temperature may show greater susceptibility to intergranular corrosion than is shown by similar metal subjected to the same test conditions but lacking cold work. The cold-worked material will, however, recover immunity sooner than annealed material either at the same or a higher sensitizing temperature.

We suggest that susceptibility to stress-corrosion cracking represents the

early stages of susceptibility to intergranular corrosion or a relatively low degree of sensitization. It is interesting to note the similarity of behavior between these results and those obtained by Schroeder and co-workers in their work on the intercrystalline cracking of mild carbon steel as used in boilers. (Cf. A.R.E.A. Bull. 404, 1938). In both types of steels intergranular cracking can be produced in cold-worked U-bend specimens immersed in a solution containing both a corrosive agent and a protective agent. In the present instance the corrosive agent is H_2SO_4 or HF while the corresponding protective agent is $CuSO_4$ or HNO_3. It appears that the protective agent effectively shields the body of each grain leaving the corrosive agent to attack the grain boundary metal. It may well be that as soon as the attack is under way the notch effect intensifies the applied stress and propagates a crack, provided the path of attack is very narrow as in the early stages of susceptibility to intergranular corrosion. However, it may be that in the more advanced stages, when the path of attack is relatively broad the notch effect may be so weakened that no crack is propagated, and the material fails eventually by disintegration of the grains.

It seems quite possible that this condition might have been revealed without the accelerating influence of cold work had the authors employed a more sensitive detector—such as the change in electrical resistance accompanying intergranular corrosion. It also appears that the authors' criterion of "sugaring" was sensitive only to the more advanced stages of sensitization, and if so it is not surprising that "cracking" and "sugaring" were not often observed simultaneously.

We believe that the rather confusing array of carbide precipitation treatments might have been materially simplified had the authors applied thermal gradient treatments to each of the strip specimens. Each specimen would then have been subjected at some point along its stressed length to every temperature at which precipitation might occur and thus the point of maximum severity would be automatically disclosed and the results made correspondingly more significant.

It seems unlikely that heats of the same stainless steel grade differ inherently one from another in their susceptibility to this phenomenon, and we suggest that these apparent differences may be related to such factors as the presence of a very small amount of grain boundary ferrite, initial condition and distribution of carbides, and austenite grain size. For example, it must be remembered that most of the steels described by the authors are what Dr. John A. Mathews once termed "marginal alloys," which may or may not be entirely austenitic depending on differences in composition, degree of hot work, heat treatment, and other factors. Thus it is not improbable that the cracking which occurred in deforming Steels 3 and 4 (Table III) is associated with the presence of delta ferrite.

Finally it should be added that if the authors observed "sugaring" in some of the titanium- or columbium-bearing alloys it must be owing to an insufficient ratio of the element to carbon, to a lack of uniform distribution of the element, or to the need of a stabilizing heat treatment. Experience has amply demonstrated that when these conditions are met the alloys are immune to intergranular corrosion.

Oral Discussion

V. N. KRIVOBOK:[1] Mr. Scheil, have you ever found that in case columbium is used in austenitic alloys it is necessary to have about ten times the carbon for stabilizing treatment?

M. A. SCHEIL: Dr. Krivobok's question regarding the columbium content in relation to the carbon content can be answered from our experience. When I referred to some of the stabilized austenitic stainless alloys (titanium and columbium) as having sugared or shown general corrosive attack in the presentation of this paper, I was referring specifically to those containing columbium about six times the carbon. In these alloys I would seriously consider heat treatment stabilization after heavy welding. I agree with you that when you have columbium up to 1 per cent with low carbon, below 0.10 per cent and preferably below 0.08 per cent, heat treatment stabilization is not necessary after welding. Thank you for bringing this up.

V. N. KRIVOBOK: Gentlemen, it was my privilege to be informed about an ingenious method of testing Dr. Hoyt and Mr. Scheil have done. Since their work, which is highly interesting and highly important, I have tried to contribute a bit in the same general knowledge. The four conditions which the authors have ably brought out, the absence of stress-strain, then the chemical stability of the alloy, probably the previous history, etc., are quite important. I should like to suggest that one of the factors which was found to be important was the grain size and it stands to reason that it would be so. Further, that in alloys, in which the stability is usually satisfactory, stability is further increased, not only by analysis but by treatment as well. You see after all these steels are not, strictly speaking, in a stable condition. When the stability is increased the sensitivity to stress corrosion seems to be decreased. I was also very much interested, if I may take one more minute, Mr. Chairman, and ladies and gentlemen, in going a bit further than that in paralleling the stress-corrosion characteristics of these alloys with a study of their general behavior, that is, the general corrosion resistance. Partly no doubt by virtue of my birth, I was very much intrigued by a publication which has recently appeared from Moscow which showed that in stainless steels at critical stress, which was measured by the amount of polar reduction, the corrosion rate went down to practically nil while with more stress or less stress the corrosion was quite high. I am sorry to say I was not able to check those results and that the general resistance to corrosion seems to be affected not only by the plastic deformation but also by the amount of elastic deformation. In that connection the ingenious methods of Dr. Hoyt and Mr. Scheil were indeed important in studying these phenomena. I have nothing to add but high praise to everything as usual to Dr. Hoyt and his associate, Mr. Scheil.

Authors' Reply

Dr. Aborn has added some very pertinent remarks to this paper by his clear conception of the anomalies of stainless steel. We welcome his discussion and will try to bring out some experimental evidence in reply:

[1]Professor of metallurgy, Carnegie Institute of Technology, Pittsburgh, and associate director of research, Allegheny-Ludlum Steel Corp., Brackenridge, Pa.

We do not believe that general intergranular attack is always necessary to develop stress cracking, although every specimen that fails by stress cracking will eventually show at some later date a general intergranular attack. While we say this without the knowledge of a very sensitive test for intergranular attack, such as Dr. Aborn's electrical sensitivity method, we have reason to believe it because on a number of different occasions we have taken field tested stress-corrosion cracked test samples and produced excellent bend tests from both halves of the fracture. If intergranular attack had been general this would not have been possible. Stress, in an alloy susceptible to stress cracking, appears to produce limited intergranular corrosion in a few selected grain boundaries producing a notch effect which propagates a crack rapidly. Fig. 12a illustrates a laboratory specimen which has shown general intergranular attack of all surface grains before the crack propagated at one particular point. The evidence from field tests points to a very limited susceptibility in the vicinity of some highly stressed area.

To say that it seems unlikely that heats of the same stainless steel grade differ inherently one from another in their susceptibility to this phenomenon is to infer that heats of the same grade and of similar chemical composition never vary in corrosion properties. It is entirely possible that "processing" may be a large factor in producing some of the factors relating to this phenomenon. However, these are usually out of the hands of the consumer and should be controlled in manufacture. It is possible that a proper balancing of the alloys could result in a decided influence toward eliminating stress cracking in unstabilized alloys, particularly of the austenitic alloys containing molybdenum.

Three $\frac{5}{32}$-inch thick plates from three different, but similar, heats of Type 316 alloys quenched at the mill were welded with a cross weld in a similar manner. One set was corrosion tested "as-welded," another, after 4 hours heat treatment at 1000 degrees Fahr., and still another after 4 hours treatment at 1200 degrees Fahr. Two of the three different heats showed attack in the heat affected zone "as-welded." The same two showed sugaring after heat treatment to 1000 degrees Fahr. in the heat affected zone while the remainder of the plate was O.K., and all three showed attack of the plate material after treatment at 1200 degrees Fahr. The three heats gave analyses as follows:

	C	Mn	Cr	Ni	Mo	Attack in heat affected zone of cross weld deposits "as-welded" and after 1000 degrees Fahr.
1.	0.07	1.58	18.94	9.68	2.37	
2.	0.07	1.38	17.02	10.46	2.40	
3.	0.08	1.32	17.53	10.32	2.43	

Steel 1 shows a few large ferrite pools not well distributed.
Steel 2 shows very small and numerous ferrite pools uniformly distributed.
Steel 3 shows small and numerous ferrite pools quite evenly distributed.

Specimens from each heat were subjected to a grain coarsening heat treatment followed by a heat treatment at 1000 degrees Fahr. for 4 hours. Specimens were then tested in the nitric-hydrofluoric acid mixture for evidences of intergranular attack. The following table records the results that were obtained in these tests:

Treatment	Steel 1	2	3
1900° F.—Air Cool + 1000° F. for 4 hours	sugared	O.K.	O.K.
2000° F.—Air Cool + 1000° F. for 4 hours	O.K.	O.K.	O.K.
2100° F.—Air Cool + 1000° F. for 4 hours	O.K.	O.K.	O.K.
2200° F.—Air Cool + 1000° F. for 4 hours	O.K.	O.K.	O.K.
2300° F.—Air Cool + 1000° F. for 4 hours	O.K.	O.K.	O.K.
2400° F.—Air Cool + 1000° F. for 4 hours	O.K.	sugared	O.K.
2500° F.—Air Cool + 1000° F. for 4 hours	sugared	sugared	O.K.

The apparent differences in the intergranular corrosion properties of the three cross-welded steels may be due to their ability to prevent harmful carbide precipitation by the differences observed microscopically and after grain coarsening experiments.

Regarding Dr. Aborn's last paragraph on the observed "sugaring" in some of the titanium- or columbium-bearing alloys we offer the following laboratory stress-corrosion test data on five different heats of these alloys made by four different steel producers. The notation following the heat treatment of the samples indicates the number of hours in the corroding media and the designation "O.K." means that no attack was observed. "Att." means that a general corrosion of the surface took place. "S" indicates "sugaring" or severe intergranular attack at the surface. Treatment (5) which was a long time heating at 900 degrees Fahr. gave an indication of superiority of one alloy over the other.

	Type 321				Type 347		
Chemical Analysis	(1)	(2)	(3)	(4)	(5)	(6)	(7)
C	0.06	0.06	0.06	0.06	0.06	0.06	0.07
Mn	0.42	0.42	0.48	0.48	0.50	0.50	0.42
Si	0.44	0.44	0.57	0.34	0.28	0.28	0.27
Cr	19.10	19.10	17.70	18.10	18.62	18.62	18.72
Ni	9.60	9.60	8.10	9.50	11.36	11.36	9.86
Ti	0.60	0.60	0.64	0.33	....	....	....
Cb	....	....	....	....	0.86	0.86	0.42

Notes: All samples were mill annealed and passivated. Samples (1) and (5) were stabilized.

Heat Treatment / Test Solution	(1) HNO_3+ HF	(2) HNO_3+ HF	(3) HNO_3+ HF	(4) Aborn's
(1) As Received—No Heat Treatment	2950/OK	2950/OK	2950/OK	1200/OK
(2) 1600° F.—2 hrs.—Fur. Cool	1780/OK	1780/OK	1780/OK	1060/Sl.S.
(3) Same as (2) + 1200° F.—4 hrs.—A.C.	1780/OK	1780/OK	1780/Att.	1060/OK
(4) 1200° F.—2 hrs.—Air Cool	1300/OK	1300/OK	1300/OK	1060/S.
(5) 900° F.—1000 hrs.—Air Cool	840/Att.	840/Att.	240/Att.	....

Heat Treatment / Test Solution	(5) HNO_3 + HF	(6) HNO_3 + HF	(7) HNO_3 + HF
(1) As Received—No Heat Treatment	2950/OK	2950/OK	2950/OK
(2) 1600° F.—2 hrs.—Fur. Cool	1780/OK	1780/OK	485/Att.
(3) Same as (2) + 1200° F.—4 hrs.—A.C.	1780/OK	1780/OK	485/Att.
(4) 1200° F.—2 hrs.—Air Cool	1300/OK	1300/OK	360/S.
(5) 900° F.—1000 hrs.—Air Cool	1780/OK	1780/OK	240/S.

The 18-8 titanium alloys with titanium equal to ten times the carbon content showed general attack in the stress-corrosion test after a heating at 900 degrees Fahr. regardless of whether the alloy was mill annealed or mill annealed and given a stabilizing heat treatment. A similar alloy with titanium equal to six times the carbon content required heat treatment stabilization of the mill annealed sample to resist sugaring after a heat treatment in the damaging range to 1200 degrees Fahr.

The 18-8 columbium alloys with columbium at least ten times the carbon content regardless of previous treatment were not affected in the stress-corrosion test when similarly heat treated at 900 degrees Fahr. A similar alloy with columbium equal to six times the carbon content could not be stabilized by heat treatment to resist attack after a heat treatment in the damaging range. The mill annealed samples showed sugaring after heating in the damaging range.

Dr. Bain has raised the question of whether low temperatures may give stress cracking. Material from the manway neck, tests of which have already been discussed in the paper, was put through the following treatments:

Four strips were heated to 1950 degrees Fahr. and water quenched. The following heat treatment was carried out:

Specimen 1—This specimen was heated in the unstrained condition 145 hours at 865 degrees Fahr. It was then formed cold to a horseshoe and stressed.

Specimen 2—This specimen was cold formed to a horseshoe and then heated the same as specimen 1 and stressed cold.

Specimen 3—This specimen was heated in the unstressed condition 10 minutes at 965 degrees Fahr. It was then formed cold to a horseshoe and stressed.

Specimen 4—This specimen was cold formed to a horseshoe and then heated same as specimen 3 and stressed cold.

All four specimens were placed in boiling Aborn's copper sulphate solution. Specimens 1 and 2 were tested for a total time of 20 days and found to be free from stress-corrosion cracking. Specimens 3 and 4 were tested for 6 days and found to be O.K. Then specimens 3 and 4 were heated at 965 degrees Fahr. for 15 minutes. The specimens were stressed during the heat treatment. After 13 days both specimens 3 and 4 were O.K. At this time specimen 3 was reheated to 965 degrees Fahr. for ¾ hour and specimen 4 was reheated at 965 degrees Fahr. for ¼ hour. Another copper sulphate test was made over a period of 16 days with no signs of stress-corrosion cracking. After this, specimen 3 was reheated to 965 degrees Fahr. for 2 hours. This was a total time of about 3 hours at 965 degrees Fahr. Also, specimen 4 was reheated to 965 degrees Fahr. for 20 hours. A test in copper sulphate showed specimen 3 to be O.K. after 7 days but specimen 4 failed by cracking first and then sugaring in 1 day's time.

These results show that low temperatures below 1000 degrees Fahr. do not produce stress-corrosion cracking in a susceptible alloy unless the period of time at temperature is sufficient to produce intergranular attack.

To answer Mr. Luger's questions we will reply as follows:

Question (1)—Two heats out of eight of the Type 316 alloys showed stress-corrosion cracking. The analyses given on page 209 were not heat analyses and the actual analyses of the failed specimens were as follows:

	C	Mn	Si	Cr	Ni	Mo
Heat producing 2 failures	0.07	0.38	0.35	18.8	11.2	3.0
Heat producing 1 failure	0.08	1.38	0.35	18.0	10.7	2.5

Question (3)—Type 316 alloys mentioned on page 217 are heat analysis.

	C	Mn	Si	Cr	Ni	Mo
Not sensitive to S-C can be desensitized by H.T.	0.07	0.37	0.30	18.1	9.4	3.21
Was sensitive to S-C not desensitized by H.T.	0.05	1.40	0.18	18.3	10.7	2.80

We agree that balancing the composition is not the answer and certainly higher carbon above 0.10 per cent is definitely to be avoided.

With all due regard to Mr. Luger's remarks concerning the cracking of the two heats of Type 316 alloy which were obtained in accelerated laboratory tests using hot nitric acid, we would like to point out that one of these heats was used in service tests which were described on page 214 and failed badly without any signs of general corrosion attack. The five different stainless alloys included in this service test were all tested together as described, under operating conditions in a sulphite digester. Steels Nos. 2, 3, and 5 showed



surface attack on all the samples tested for the full 650 hours. Steels Nos. 1 and 4 containing molybdenum showed no tendency toward surface attack and were absolutely bright when removed after 650 hours. The molybdenum bearing austenitic alloys have enjoyed a good reputation for general corrosion resistance in sulphite service.

We agree with Mr. Luger on the advantages of the electrical resistivity method for detecting slight intergranular attack. This method is so sensitive that we have found it necessary to obtain increases of the order of 100 per cent before "sugaring" is apparent.

The tests conducted on materials given in Table III have indicated that single pass welds on 11 gage sheet have not shown attack or stress cracking in the "as-welded not subsequently heat treated" condition which is Treatment No. 8. However, other conditions might cause corrosion alongside the weld band and we would point out the data refer specifically to stress-corrosion cracking. As an example of this, Steel No. 1 was welded with a cross weld and showed complete failure in the heat affected zone adjacent to the welds in the as-welded condition. (See Fig. above.)

Steel No. 3 may have cracked due to copious amounts of high temperature ferrite. However, sample (2) was cracked while deforming at 1950 degrees Fahr. and sample (6) was heated to 1200 degrees Fahr. and deformed at a red

heat. Other samples such as (1) were deformed cold in the as-received condition O.K.

Mr. Luger brings up an interesting observation in his discussion of stress-cracking phenomena in properly heat treated 18-8 alloys that became pitted due to the presence of halides in the corroding media. Mr. W. Brooks has proposed some similar circumstances, namely, that stress cracking can occur due to stress concentration at notches produced by corrosion pits as well as by intergranular corrosion. During our laboratory testing we produced considerable pitting in titanium and columbium stabilized alloys by a very long time corrosion test in the nitric-hydrofluoric acid mixture. Many of these specimens had been heated within the damaging range, were cold formed, stressed, and then tested as long as 3200 hours. During the latter 1000 hours pitting developed as well as considerable general corrosion but in no cases did we observe stress cracking. Several of these pitted specimens were bent 180 degrees after their corrosion test and still exhibited excellent ductility on the pitted surfaces. An 18-8 steel air quenched from 1950 degrees Fahr. was treated similarly and developed pits during testing, but after 3200 hours did not show any signs of stress cracking. We do not have laboratory data at present which would substantiate pitting alone as a direct cause of stress cracking. It is possible that the pitting referred to may have been associated with the grain boundaries.

THE EFFECT OF TYPE OF COLD DEFORMATION ON THE RECRYSTALLIZATION PROPERTIES OF ARMCO IRON

By Herman F. Kaiser and Howard F. Taylor

Abstract

The recrystallization of Armco iron when cold-deformed by torsion, elongation in tension, and rolling, and subsequently annealed, has been studied with care taken to keep variables other than the type of deformation as alike as possible. From the data in each case a recrystallization diagram was constructed. It was found possible to relate the critical degree of deformation at any chosen annealing temperature for the three different types of cold deformation by expressing the degree of deformation either in terms of specific shear or better (following Nadai), in terms of octahedral shear. Experiments on the effect of time of anneal were also carried out.

THE study of the various factors which determine the grain sizes and structures of metals which have been cold-worked and annealed started about ninety years ago and considerable work has been done in the past twenty years. Some of this work has been done because of the growing scientific interest in single crystals of metals; some because of the industrial importance of avoiding the production of coarse crystalline products in the working and fabrication of metals; and some for sundry and scientific purposes.

The purpose of the present work is a study of the type of deformation in relation to the process of recrystallization on annealing after cold work. Three types of deformation were studied; shearing deformation in a twisted bar, elongation in tension, and compression in rolling. For each case a "recrystallization diagram" was determined with the experimental conditions as nearly alike as was feasible. In addition, various special experiments were carried out to gain an insight in the influence of several other factors which are operative in the phenomena of recrystallization. The two chief factors which determine the grain size which results in a piece of

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metal when it is cold-worked and subsequently annealed are the degree of deformation and the temperature of annealing. It is quite obvious that in spite of the importance of these two factors there are other factors involved, such as the time of annealing, the kind of mechanical deformation, the temperature of deformation, the concentration and nature of impurities in the metal, the grain size and structural peculiarities of the starting material, the previous history of the material, and so on. The nature and number of these factors almost discourages a comprehensive complete treatment of this subject even for a single metal but at least something may be accomplished by concentration of experiments on particular factors.

A brief historical review of work done on the recrystallization of iron and steel will not be out of place here.

In 1858 Nogues(1)[1] made mention of a coarse crystalline structure that appeared in platinum wire netting heated for days in a reducing gas flame and showed that this was true on the wire cross section as well as on the surface. The only conclusion he drew was that the high temperature exerted an influence on the molecular structure of the platinum.

In the next twenty years nothing further was done until in 1881 the observations of an obscure worker, Kalischer (3), were published. However, in this interval appeared the work of Sorby (2) inaugurating the beginning of metallographic examination of metals, but not until some time later did Sorby (5) publish work on recrystallization. Kalischer recognized that not only the temperature of annealing but the deformation itself were factors. Kalischer made experiments on quite a range of technical metals including iron. In 1883 Ledebur (4) and later others working with iron and other metals showed that the time of annealing exerted an even greater influence than the temperature of annealing. Ledebur used wrought iron and noticed the production of a very coarse crystalline structure from the previously "fibered" rolled structure. This fact was verified by Sauveur (6) in 1893, by Stead (7) in 1898, and still later in 1913 by Moellendorf and Czochralski (21). Stead (7) called attention to a brittleness sometimes termed "Stead's brittleness" in rolled and annealed sheet iron, which brittleness is caused by the formation of a very coarse-grain structure. Czochralski (82) has drawn up a very interesting historical summary of this early work which may be consulted for further details in this field. In 1915 Chappell (25) pub-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

lished a classic paper on the recrystallization of iron in which he carefully took into consideration a number of factors including degree of deformation, temperature and time of annealing, and carbon content and carefully followed the course of recrystallization with increasing temperature, observing the lowest temperature of recrystallization. In 1916 Czochralski (82) published a paper on the recrystallization of tin in which he introduced the idea of graphically representing the results of a recrystallization study by means of a space diagram, that is, a rectangular co-ordinate system where the co-ordinates are grain size, degree of deformation and annealing temperature. Although this has limited application it has found extensive use during recent years in presenting recrystallization studies. In 1918 Oberhoffer and Oertal (45) developed a recrystallization diagram for electrolytic iron following Czochralski and in 1920 Oberhoffer and Jungbluth (35) developed a similar diagram for commercial iron. For commercial iron they found, as did Pomp (33), that the grain size appeared to be a maximum for a cold deformation of about 10 per cent reduction in height, a phenomenon which they did not find in the case of electrolytic iron. They also found that the grain size was dependent on the time of annealing. What they described as a peculiarity in commercial iron probably is not a peculiarity at all. For all metals there is a degree of plastic deformation termed the critical deformation below which no marked grain enlargement takes place at a given temperature of annealing. In commercial iron this is greater than in electrolytic iron.

Following upon this came the work of Hanemann and Lucke (46) introducing a new departure from previous methods of study. They studied the grain size which appears in metals when worked at various temperatures. In previous work the deformation was carried out cold and this left the temperature of deformation as an uncertain variable. Their procedure combined the temperature of annealing with the temperature of working. Some very interesting results have been obtained by following such methods. Their results are also expressed in the form of recrystallization diagrams.

The work in recrystallization has since been carried out in varied directions. Hanemann and his co-workers have applied their method of study to the hot rolling process (72). Considerable interest has risen in the past years in iron single crystals and their properties, especially their magnetic properties. The finding of the necessary conditions for producing iron single crystals has led to various works

(44, 52, 57, 60, 68, 73, 74 and 81) allied to recrystallization. Another stimulus has been the question of the relation between magnetic properties and the grain size and some work (68, 69 and 81) in recrystallization has been carried out for this purpose, such as that of Moos, Oberhoffer and Oertel (69) who studied the recrystallization of transformer steel sheet.

Other scientific problems have called for special studies, such as orientation of crystallites produced in deformation and annealing (52, 60, and 75), internal stresses in metals (49, 59, and 78), the effects of hydrogen on the recrystallization of electrolytic iron (53, 50, 48, 36, and 71), peculiarities in the microstructure of ferrite (65, 70), etc. Particular studies have been made in regard to the structure of rolled sheet products (54, 66, 75, 76, 77, and 79). Ahrell (63) has made a study of the recrystallization of 0.11 per cent carbon cold drawn steel tubing. He has expressed his result in conventional diagram form and in addition has brought out the rather interesting result that the time of annealing becomes more and more important the smaller the degree of deformation.

Space does not permit a lengthier discussion of the work done on the recrystallization of iron and steel, especially that of the past few years, and therefore a bibliography intended to be as comprehensive as possible has been appended to this paper.

Recrystallization of Armco Iron Deformed by Torsion

Material and Mechanical Deformation—The material used in this work was 1-inch round Armco iron bar stock. Two lots were received having the composition given below:

	Lot 1 Per Cent	Lot 2 Per Cent
Carbon	0.015	0.011
Manganese	——	0.012
Phosphorus	0.008	0.004
Sulphur	0.027	0.028
Copper	——	0.041
Silicon	0.008	——

While these compositions are practically the same, Lot 2 is probably of higher purity, for less inclusions were noted in it. The material was sawed into bars about 11 inches in length which were turned smooth to a diameter of $\frac{15}{16}$ inch. (See Fig. 4(a)). These were then packed in asbestos, heated 3 hours at 930 degrees Cent. (1705 degrees Fahr.) and cooled in the furnace.

Light reference lines for subsequent measurement of the amount of permanent torsion were engraved upon the bars. The bars were then twisted various amounts in a torsion testing machine. The amount and uniformity of the torsion in each case was determined from measurements on the engraved lines on the bars. The torsion was surprisingly uniform. A bar (Specimen B) from Lot 1, representing a range of specific shear, 0 — 0.125 per cent, equivalent to a range of elongations 0 — 11.5 per cent, was selected for further study. This bar, which furnished the data of Table I, was sawed into cylindrical samples ½ inch in height.

Annealing Treatments—The cylindrical samples were annealed at the following experimental temperatures: 300, 400, 500, 600, 700, 760, 780, 800, 825, 850 and 875 degrees Cent. (570, 750, 930, 1110, 1290, 1400, 1435, 1470, 1515, 1560, 1605 degrees Fahr.). The time of annealing was generally taken at 3 hours except where specified otherwise in Table I. To eliminate the effects of annealing at temperatures other than those here studied, it was decided to carry out the heating operation as rapidly as possible and thus the sample wrapped in copper foil (to minimize surface oxidation) was dropped into a hole in a massive copper block held in the furnace at the desired temperature. At the end of the annealing period the sample was quenched.

Metallographic Studies—In the initial part of this work each specimen was examined both on sections through and perpendicular to the bar axis; but upon finding that the structures produced by the annealing treatment were equiaxed, only the normal sections were used in later studies. Photomicrographs were taken on the prepared normal section at different distances from the center both before and after annealing. These served to determine the grain size by the usual counting method. In those samples where the largest grains were very large, the largest grain sizes were determined from grain counts between concentric circles drawn upon a macrographic view of the whole section.

Effect of Annealing Time—A study of the effect of the annealing time was made by taking microviews of a Lot 1 section, prepared after annealing for 20, 40, 90 and 170 minutes at 825 degrees Cent. (1515 degrees Fahr.). No appreciable differences in these were noted, leading to the conclusion that the chosen annealing period of 3 hours was ample to insure full recrystallization. Later, however, a specimen from Lot 2 annealed for 15 minutes under like conditions

Table I

Grain Size Data from Torsion Bar Study

Annealing Temp. °C	Annealing time Hrs.	Radii mm. r	Av. Gr. Size before Anneal*	Av. Grain Size after Anneal	Sp. Shear $\gamma = \frac{r\theta}{l} = r \times .02083$
300	3	3	3.5	4.7	0.063
		6	4.6	4.9	0.125
		9	4.2	6.3	0.188
400	3	0	4.7	4.1	0.000
		3	4.8	—	0.063
		4	—	4.3	0.083
		6	4.0	—	0.125
		8	—	4.5	0.167
		9	4.8	—	0.188
		11	—	6.0	0.229
500	3	0	4.8	—	0.000
		2	—	4.6	0.041
		3	4.0	—	0.063
		5	—	5.4	0.104
		6	4.8	—	0.125
		8	—	5.5	0.167
		10	4.6	—	0.208
		11	—	4.8	0.229
600	3	2	4.8	5.2	0.041
		5	—	5.9	0.104
		6	4.0	—	0.125
		8	—	5.4	0.167
		10	5.7	—	0.208
		11	—	6.6	0.229
700	3	2	4.6	5.1	0.041
		5	5.4	5.9	0.104
		8	5.6	6.7	0.167
		11	6.9	7.9	0.229
760	3	.5	5.8	—	0.010
		2	—	5.8	0.041
		5	5.8	—	0.104
		7.5	—	8.4	0.156
		8	5.5	—	0.167
		9.5	—	9.9	0.198
		11	5.5	—	0.229
		11.5	—	8.7	0.240
780	3	3.5	—	28.1	0.073
		4.5	—	27.5	0.094
		4.9	10.7	—	0.102
		5.5	—	39.0	0.115
		6.5	—	48.1	0.136
		7.5	—	49.0	0.156
800	3	2	6.0	—	0.041
		4.3	—	8.0	0.090
		5	6.0	—	0.104
		5.3	—	723	0.111
		5.4	—	684	0.113
		6.7	—	254	0.139
		8	10.0	34	0.167
		9.3	—	17	0.194
		10.7	—	16	0.223
		11	8.0	—	0.229

All the above data were obtained from Bar Specimen B, Lot 1.

*Grain sizes given in Sq. microns x 10^{-8}. The lowest grain size is around ASTM No. 5, the largest reported greater than No. 0.

Table I (cont'd)
Grain Size Data from Torsion Bar Study

Annealing Temp. °C.	Annealing time Hrs.	Radii mm. r	Av. Gr. Size before Anneal*	Av. Grain Size after Anneal	Sp. Shear $\gamma = \frac{r\theta}{l} = r \times .02083$
825	3	1.7	—	17	0.035
		2.0	6.0	—	0.041
		3.2	—	13	0.067
		4.5	—	21	0.094
		5.0	7.0	1135	0.104
		6.0	—	180	0.125
		7.4	—	75	0.154
		8.0	8.0	—	0.167
		8.9	—	63	0.185
		10.0	—	30	0.208
		11.0	6.0	—	0.229
		11.4	—	17	0.238
850	3	2.0	6.0	—	0.041
		3.9	7.0	—	0.081
		4.3	—	2000	0.090
		4.8	—	225	0.100
		5.0	6.0	—	0.104
		7.8	—	47	0.163
		8.0	8.0	—	0.167
		10.8	9.0	19	0.225
875	3	1.6	—	9	0.033
		2.0	11.0	—	0.041
		3.9	—	220	0.081
		4.4	—	1570	0.092
		5.0	10.0	—	0.104
		5.9	—	133	0.123
		7.9	—	52	0.165
		8.0	10.0	—	0.167
		9.2	—	30	0.192
		10.5	—	19	0.219
		11.0	10.0	—	0.229
		11.5	—	21	0.240

Critical Radii of Recrystallization—

Temp. °C.—Below	760	760	780	800	825	850	875
Radii, mm.	—	10	8	4.5	4.1	4.0	2.8
Sp. Shear	—	0.208	0.167	0.094	0.085	0.083	0.058

failed to show a complete structure, so 15 minutes should not be looked upon as sufficient. The metallographic data obtained have been summarized in Table I, and these data have been used to construct the recrystallization diagram shown in Fig. 1. Fig. 2 shows typical microstructure observed in the torsion specimens from Bar B, Lot 1, annealed at 780, 825 and 875 degrees Cent. (1435, 1515, 1605 degrees Fahr.). It must be mentioned here that the curves shown in Fig. 1 represent averages of the grain size data from which single determinations of the grain size may differ somewhat. This is especially true for the data corresponding to the lower annealing temperatures 780 degrees Cent. (1435 degrees Fahr.) and below.

These show clearly how the critical deformation decreases as the annealing temperature increases and also how much more poorly defined the critical degree of reduction becomes at lower annealing temperatures. It may also be noted on these sections that there are regions where the recrystallization did not take place, especially in the specimen annealed at 780 degrees Cent. (1435 degeres Fahr.). Although the ring of largest grains is not very distinct, it appears at a fairly definite position radius. This effect may be due to a non-uniform distribution of the impurities in the metal, causing some regions to behave differently from the rest, but an annealing time study at 825 degrees Cent. (1515 degrees Fahr.) showed that there was little change in the shape and size of these areas as the annealing time was increased from 20 minutes to three hours.

In the diagram of Fig. 1 the vertical portions of the curves for 800 degrees Cent. (1470 degrees F.) and higher were located to show as closely as possible the minimum shear at which large grains were formed. For the 780 degrees Cent. (1435 degrees Fahr.) curve this line could not be drawn because the grain sizes tapered to a maximum over a range of radii. It should be noted that the curve for 760 degrees Cent. (1400 degrees Fahr.) shows a slight peak, corresponding to a specific shear around 0.10.

Since the point of main interest in this work was always the effect of a particular annealing temperature on a particular mechanical deformation, no study of the rate of heating was attempted. Low heating of the specimen would have meant exposures for appreciable lengths of time to annealing temperatures other than the particular one being studied. Although this does not preclude the possibility that the rate of heating may influence the results in this work, a uniform technique of rapid heating was followed.

The effect of time of heating was at first studied only at 825 degrees Cent. (1515 degrees Fahr.) and led to the conclusion that the results would be about the same in the range ½ hour to 3 hours. However, it might be suggested that annealing for long periods of time at lower temperatures might bring about effects not noticed in the initial work. This proved to be so and some results obtained will be described and discussed later in their proper connection.

A factor that could not be studied or controlled well in this work was the initial grain size. Although a much smaller initial grain size would have been welcome, that obtained here was probably as small as could be hoped for after the necessary normalizing treat-

ment to remove, as far as possible, the effects of previous history.

To make sure that the data given in Table I are truly characteristic of the material, two torsion bars with different degrees of maximum shear were prepared from Lot 2 stock. Samples from these

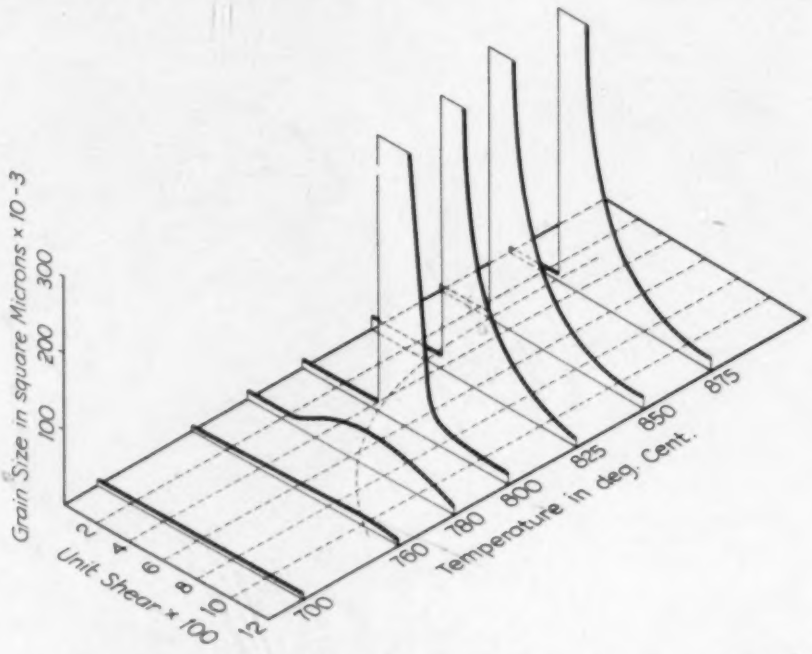


Fig. 1—Recrystallization Diagram for Armco Iron as Determined by Studies on Torsionally Deformed Bars.

were annealed as before at 780, 800 and 850 degrees Cent. (1435, 1470, 1560 degrees Fahr.) and the resulting structures obtained are shown in Fig. 3. The critical deformation given by the critical radii in the two bars are in substantial agreement with each other and also with that obtained from the bar of Lot 1. This agreement will be illustrated again later in connection with the correlation of critical degrees of deformation in various types of cold work, as may be seen in Table V A.

Recrystallization of Armco Iron Deformed in Tension

Material—The material was Lot 2 Armco iron. This was machined into nine bars of the dimensions shown in Fig. 4(b).

Preliminary Heat Treatment—The bars were wrapped in copper foil and an additional wrapping of asbestos paper. Since the material in the stock condition showed an unsatisfactory grain structure, coarse grains being interspersed through the finer grained matrix, it

was heated back and forth through A_3 for about three-quarters of an hour. This treatment produced a structure which was fairly uniform.

Deformation—In order to measure the amount and also the uniformity of elongation, scratches were spaced one-half inch apart on the surfaces of the bars. This spacing was carried out by means of

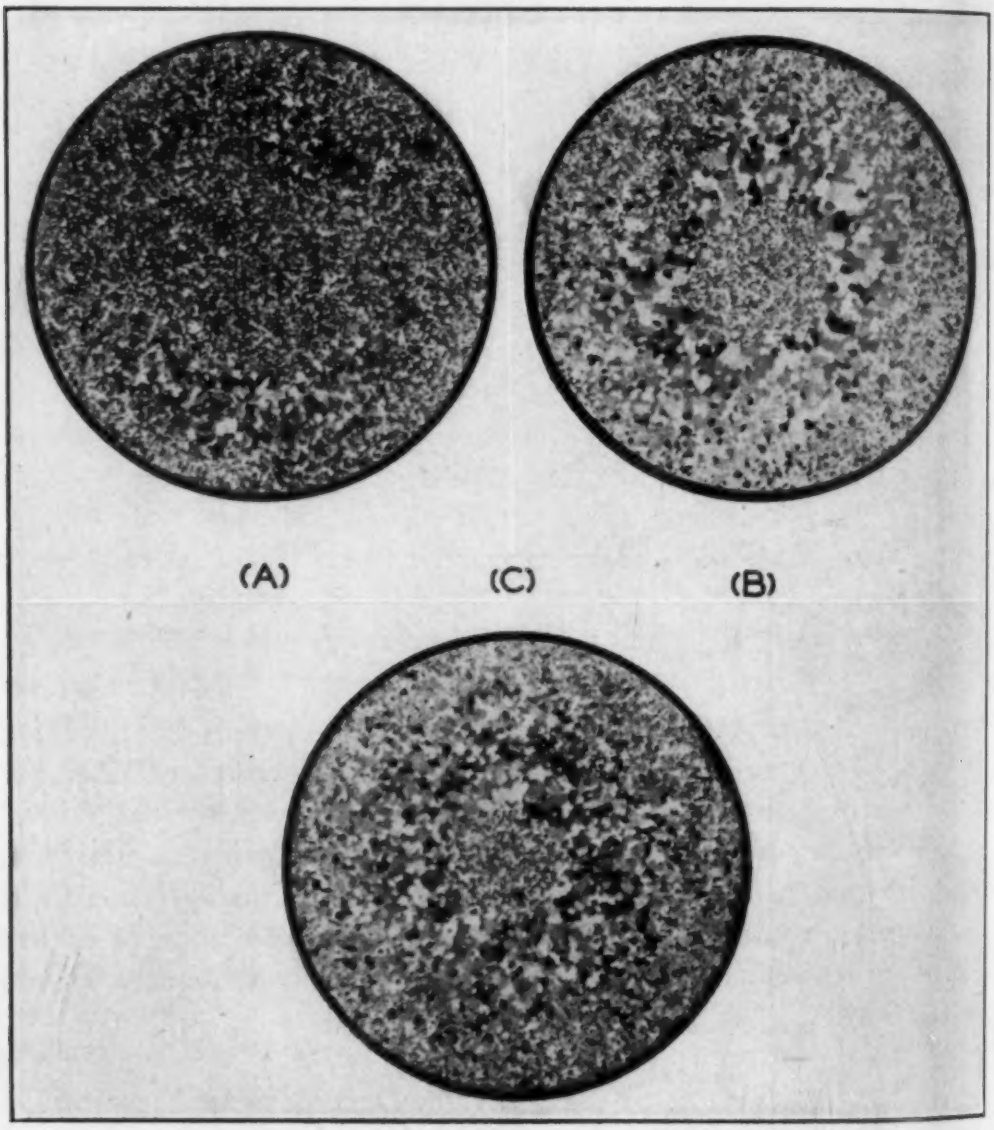


Fig. 2—Macrographs of Torsion Bar Samples After Annealing (A) 780 Degrees Cent., 3 Hours; (B) 825 Degrees Cent., 170 Minutes; (C) 875 Degrees Cent., 2 Hours.

the dividing screw of a lathe. The bars were then elongated in a tensile-testing machine to approximately 2, 4, 5, 6, 8, 10, 16 and 20 per cent elongations. Then the elongation and the uniformity of the elongation in the bars were measured by means of a comparator.

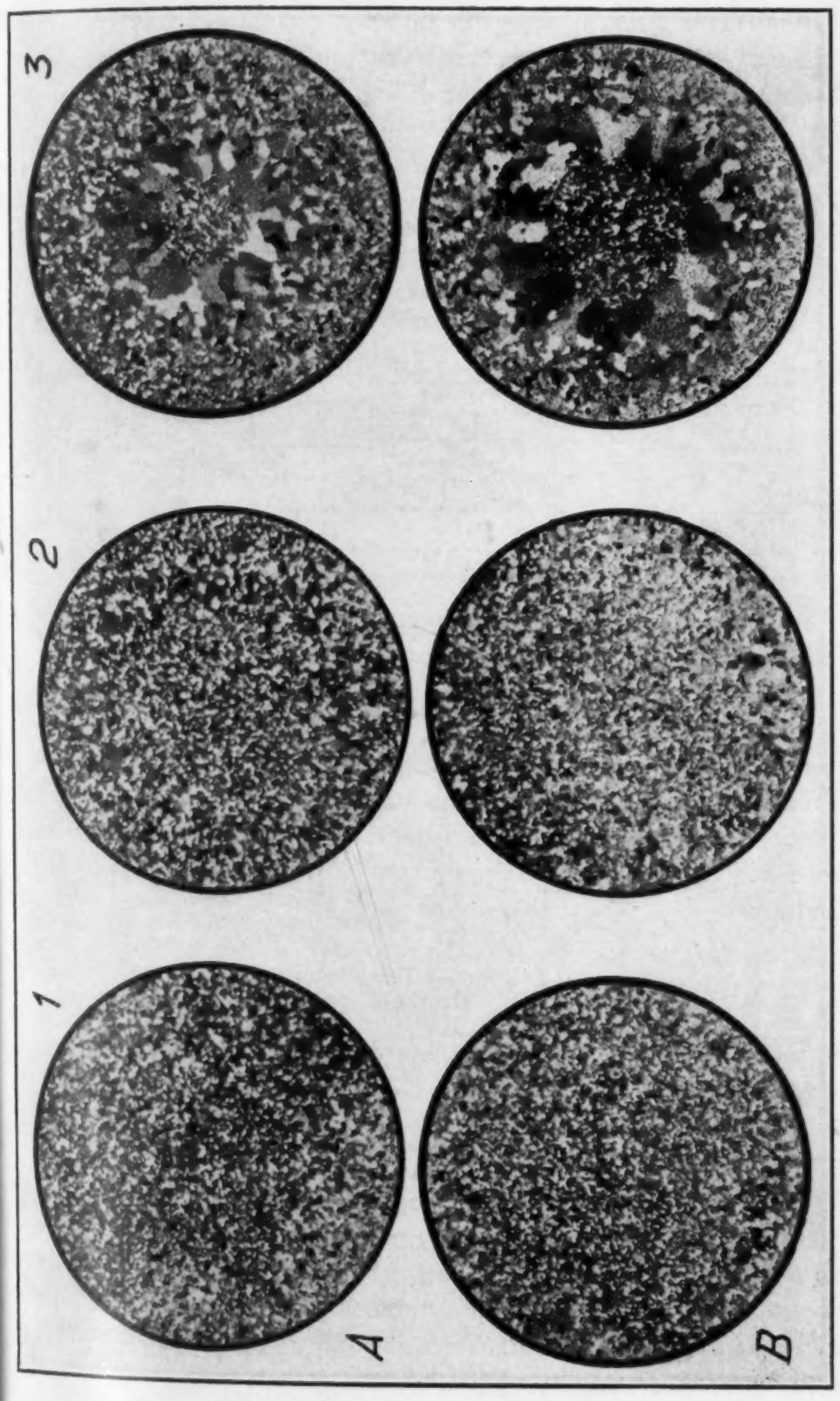


Fig. 3—Macrographs of Torsion Bar Samples from Two Bars Subjected to Like Annealing Treatment. Column (1) 780 Degrees Cent., 3 Hours; (2) 800 Degrees Cent., 3 Hours; (3) 850 Degrees Cent., 3 Hours; Top Row, Bar A $\nu = \gamma \times 0.0235$ Radians Per Millimeter. Bottom Row, Bar B $\nu = \gamma \times 0.0154$ Radians Per Millimeter.

Final Heat Treatment—Although the elongation was found to be uniform, the division of the material for heat treatment was carried out according to a system. Fig. 4 shows the manner in which the samples were lettered. Each sample (about ½ inch in length) was punch marked with the number of the bar and the

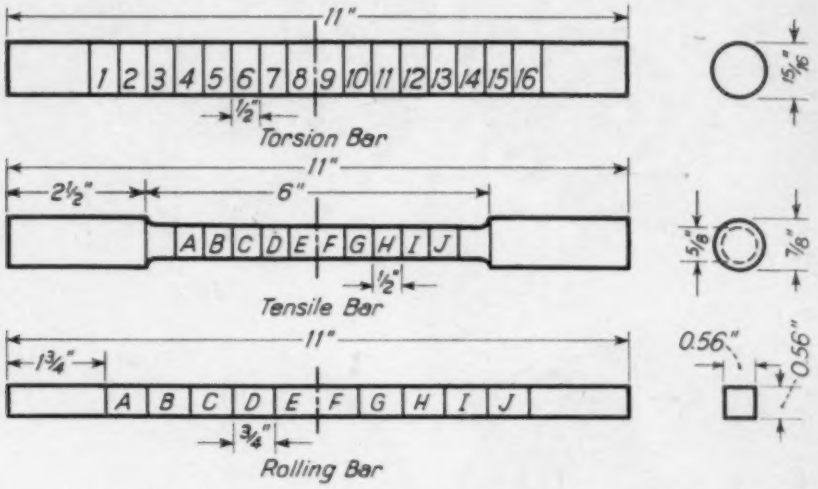


Fig. 4—Initial Dimensions of Samples. A. Torsion Bar. B. Tensile Bar. C. Rolling Bar. Transverse Lines Indicate Manner of Taking Samples.

letter indicating the position in the bar according to the above sketch. The marking preceded the division of the bars into samples. The "G" samples from each bar were reserved for the comparison of the cold-worked stages. The other samples were heat treated according to the table below:

Sample	Annealing Temperature Degrees Cent.	Time Hours
E (all bars)	875	1½
F (all bars)	825	2½
H (all bars)	780	2½
D (all bars)	760	2½
I (all bars)	700	2½

Microscopic Work and Photography—The grain size was measured on the cross section of each sample. Usually four measurements spaced at about equal intervals across the diameter were taken. In the case of samples manifesting coarse grains, it was frequently noticed that many small grains were located in the grain boundaries of the large grains. Making a grain count gave a result which could give no hint of the size of the large grains. Therefore in such

cases grain counts were also made in which the grains having a cross section small compared to that of the larger were ignored.

After the grain count work was completed, photomacrographs were taken of the cross sections of all the annealed samples. The purpose of this work was not only to get a series of representative views of typical structures resulting from the annealing, but also to study the effect which the superimposed deformation of punch marking had upon the samples.

Table II

Summary of Grain Count Data, Tension Strained and Annealed Armco Iron

Annealing Temperature: Degrees Cent.	Per Cent Elongation 1.1	3.46	4.72	6.14	7.83	8.63	15.93	19.90
700	4.42	5.60	6.51	3.31	5.56	4.19	5.05	6.30‡
760	3.56	3.50	4.25	5.34	10.13	8.91	4.23	5.80
760*	—	—	—	—	38.00	27.07	—	—
780	3.37	5.83	5.35	5.46	52.8	7.30	5.18	6.96
780*	—	—	—	10.24	—	47.9	—	—
825	3.94	3.90	43.04	54.35	47.65	15.42	4.10	5.48
825*	—	—	219.2	108.5	—	35.71	—	—
875	3.72	4.76	139.4	100.7	55.0	46.9	5.12	5.71
875*	—	—	—	—	—	—	—	—

‡All grain sizes given in square microns x 10^{-3}.

*Grain counts made neglecting the relatively small grains.

Critical Reductions** Corresponding to the Annealing Temperature.

Annealing Temperature	875	825	780	760	700
Critical Reduction	4%	4%	6.2%	7%	—

**These values except the one for 780 degrees Cent. were taken as the mean of the two lowest percentages of reduction between which there is a marked change in grain size. That for 780 degrees Cent. was chosen as the smaller value because at this value a noticeable increase in grain size was observed.

Discussion of Results Obtained in Tension Work—The data obtained has been plotted in a recrystallization diagram shown in Fig. 5 for comparison to the diagrams obtained from the other experiments. The difficulty of making a satisfactory grain count on the specimens because of the presence of numerous fine grains in the grain boundaries made necessary, as mentioned before, a separate grain count in which the grains of comparatively small cross section were not counted. For the samples annealed at 875 degrees Cent. (1605 degrees Fahr.) this procedure was not required but for those annealed at lower temperatures it was quite necessary in order to show what the size of the largest grains produced by the mechanico-thermal treatment really was. The curves corresponding to each an-

nealing temperature except 875 degrees Cent. (1605 degrees Fahr.) have been modified and the modified form of the curve used to plot the space diagram.

Fig. 6 shows a set of macro-views for series E tension-strained samples annealed at 875 degrees Cent. (1605 degrees Fahr.) for 1.5 hours. An inspection of the photomacrographs will show that the

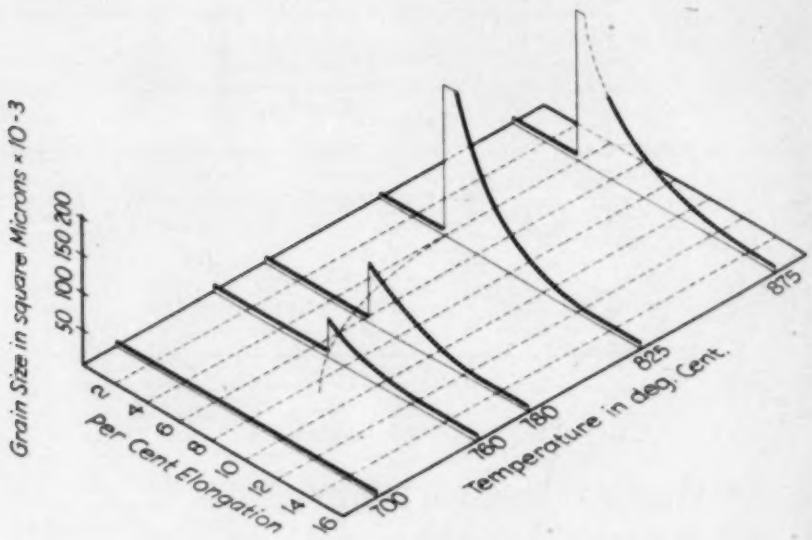


Fig. 5—Recrystallization Diagram for Armco Iron as Determined by Studies on Tensile Bars.

above arbitrary procedure was quite justified in order to get a true picture of the size of grains that will result in any particular treatment. These pictures also show the effect that punch marking the specimens had upon the recrystallization structure. This effect seems to vary from sample to sample.

In the diagram constructed the critical values were more or less arbitrarily chosen as mean values of two deformations between which there occurred a marked change in the grain size. Therefore an inspection was carried out of all the photomicrographs taken in this work to note the degrees of deformation between which the structure passes from the worked to the non-worked state for any particular annealing temperature.

The results of the above inspection regarding the critical strain corresponding to each annealing temperature have been summarized in Table III and compared with estimates made from the grain size data and from an inspection of the photomicrographs of the complete sections. The agreement is close enough but there always re-

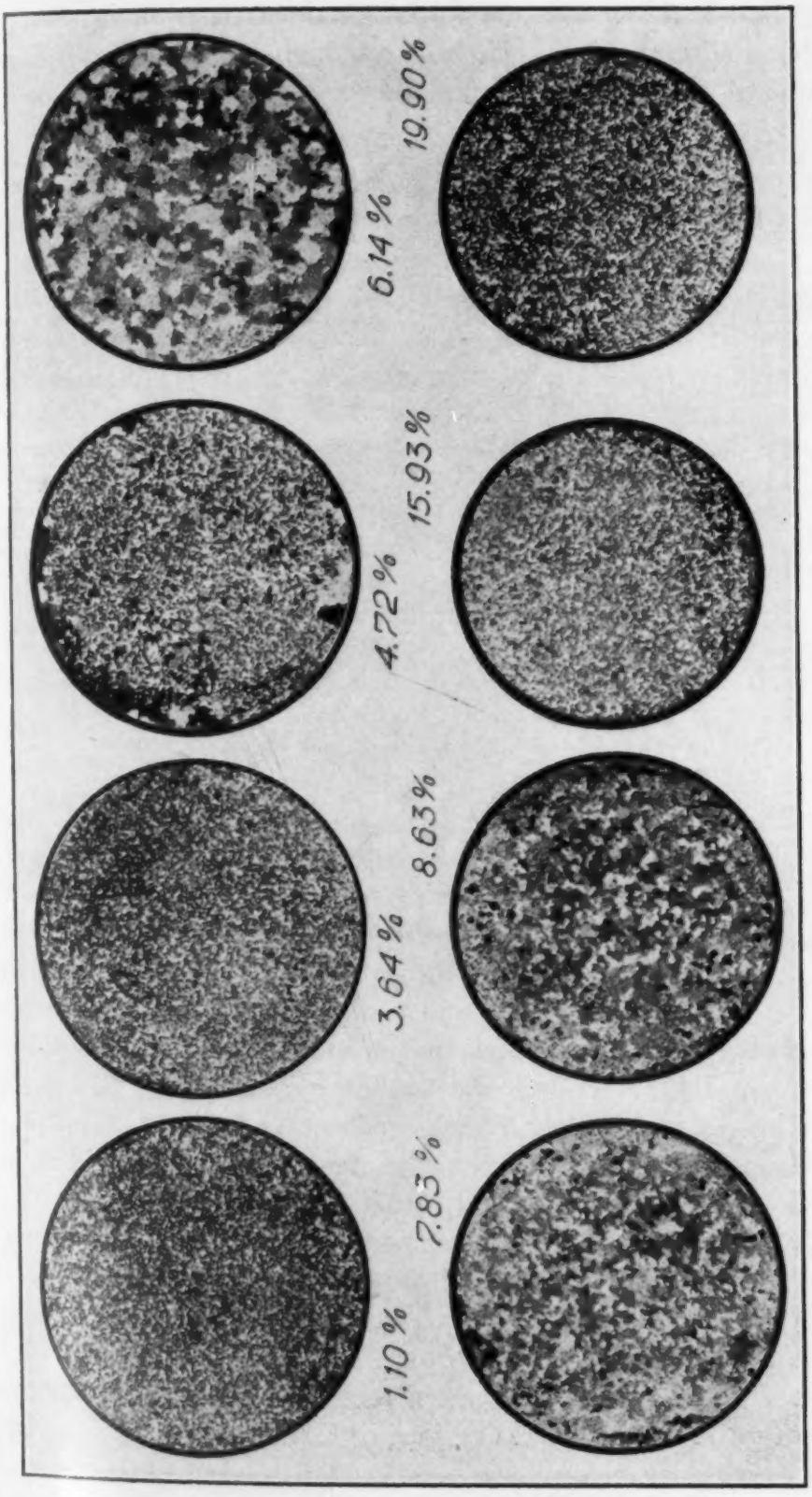


Fig. 6—Macrographs of Tensile Specimens Elongated Amounts Shown and Annealed at 875 Degrees Cent. 1.5 Hours. (Series E).

mains the possibility that the values obtained from an inspection of the photomicrographs are slightly too high because of a misinterpretation of the appearance of sections. That is, what may seem to

Table III
Critical Deformations Corresponding to Each Annealing Temperature

Temperature Degrees Cent.	Critical Elongation Per Cent Judged by Grain Size Data	Judged from Photomicrographs	Judged from Appearance of Photomacrographs
875	3.46 — 4.72	3.46 — 4.72	3.46 — 4.72
825	3.46 — 4.72	3.46 — 4.72	3.46 — 4.72
780	6.14	6.14 — 7.83	about 7.83
760	7.83 — 8.63	about 7.83	about 7.83
700	19.9 (?)	—	10%

be a cold work structure may in reality be an initial grain decomposition preceding recrystallization. In the above inspection this difficulty was kept in mind but the structures accepted as completely recrystallized were those in which no trace of either cold work or incipient grain decomposition could be seen.

Recrystallization of Rolled Armco Iron

Initial Heat Treatment and Preparation of Materials—Round bar stock (Lot II) of 1-inch diameter was machined into square bars ⅝″ x ⅝″ x 12″. These were wrapped in several thicknesses of copper foil and a layer of asbestos. The material was introduced into an electric muffle furnace at about 870 degrees Cent. (1600 degrees Fahr.) and was heated and cooled several times through A_3 as in previous work. The upper temperature attained was 923 degrees Cent. (1695 degrees Fahr.) and the lower temperature 875 degrees Cent. (1604 degrees Fahr.). After heating between these limits several times during 1½ hours the material was finally furnace-cooled down to 910 degrees Cent. (1670 degrees Fahr.).

This treatment did not produce satisfactory conditions in the material. Therefore another treatment was given in which the material was kept at 923 degrees Cent. (1695 degrees Fahr.) for two hours, the idea being to cause growth of the fine grains caused by the transformation and thus equalize out the grain size contrast. This treatment caused excessive grain growth in spots. The material was therefore again heated 923 degrees Cent. (1695 degrees Fahr.) and allowed to cool to 893 degrees Cent. (1640 degrees

Fahr.). This was repeated about three times. The resulting material showed on examination a structure which although not entirely uniform was acceptable.

The above operations caused enough oxidation of the surfaces of the bars to make necessary a light regrinding of two parallel surfaces in order to make an accurate determination of the percentage reduction in rolling.

Deformation—The samples were all cold-rolled by several passes through rolls of about 12 inches in diameter. The work was started with the smallest required reduction and subsequent pieces were rolled on their first pass to the final required thickness of the previous sample and were finished by two to six more passes through the rolls. The samples requiring the greater reductions were thus rolled down in much severer steps. Micrometer readings of the thickness of the samples were taken before and after rolling at several points along the bar, and their averages were used to compute the actual per cent reduction of the bars. The thickness of all of the bars before rolling was very close to 0.565 inch. In the rolling it was attempted to obtain certain percentages reduction. These are listed below along with the percentages obtained.

Expected Per Cent :	1	2	3	4	6	8	10	15	30
Obtained Per Cent :	0.70	1.74	2.98	4.15	5.99	8.02	10.05	14.71	29.82

Final Heat Treatment—After rolling, the bars were cut up according to the plan shown in Fig. 4 by means of a slow band saw, the specimen being kept cool during the sawing by an air blast.

The samples were heat treated according to the table below:

Sample	Annealing Temperature Degrees Cent.	Time Hours
A (all bars)	875	3
B (all bars)	850	3
C (all bars)	825	3
D (all bars)	800	3
E (all bars)	780	3
F (all bars)	760	4
J (all bars)	Not annealed	—

The samples were wrapped in copper foil and introduced into the furnace at the required temperature. A piece of plate copper, ¼ inch thick, formed the floor of the furnace. At the end of three hours the samples were removed from the furnace and cooled in air.

Each sample was cut across the direction of the bar at a position half-way between the original cut ends of the sample. This cut surface was used for microscopic examination.

Microscopic Examination and Grain Size Determination—To minimize labor and expense, photomicrographs were not taken so extensively as they were in the experiments on Armco iron deformed in tension. Photomicrographs were taken of each of the worked samples (Series J) and used in determining grain size of these samples but for all other samples grain size counts were made on the ground glass of the metallographic camera. However, each sample was carefully examined over its whole section to note peculiar features. In some of the samples large grains appeared in isolated places on the sample or in groups in certain regions of the section.

To measure the sizes of these large grains they were traced on the camera back and their areas obtained by means of a planimeter. As in the work on tension-strained Armco iron it was noted that fine grains often coexisted with very large grains. The planimetric tracings did not take these into account and thus gave a measure of the sizes of the largest grains formed. Grain size measurements were made as exactly as possible on each specimen, in the center of the section and slightly to each side of the center. The grain size and structure data for these experiments is somewhat more involved than in the experiments on pieces strained in torsion and elongation. The data are arranged below in Table IV to give not only the exact grain size values determined at the centers of the sections but also structural peculiarities and sizes of large grains. Fig. 7 shows the recrystallization diagram constructed from the data. Here the planimetrically determined grain sizes are presented.

Discussion of Results—In this work the same sort of difficulty in grain size determination appeared that was found in the work on tension strained Armco iron. As before, there was also noted nonuniformity of the recrystallization structure for the smaller degrees of deformation. It was found that rather small reductions of 3 and 4 per cent were sufficient to cause the appearance of very large grains just below the rolling surface of the piece. Then as the percentage reduction was increased, the large grains began to be formed on the sides of the section as well as just under the surface. On increasing the deformation, there appears an inversion of the structure. Large grains appear at the center of the section while the borders are relatively small grained. As the deformation is still further in-

Table IV

Grain Size Data Obtained From Rolled and Annealed Armco Iron Samples

Annealing Temperature Degrees Cent.	Percentage Reduction	Grain Size at Center ($\mu^2 \times 10^{-3}$)	Sizes of Largest Grains ($\mu^2 \times 10^{-3}$)	Remarks
875	0.70	19.76	...	Unrecrystallized.
875	1.74	21.54	...	Unrecrystallized.
875	2.98	17.64	...	Large grains appear near surface.
875	4.15	20.08	...	Large grains appear near surface.
875	5.99	21.57	606	Large grains in surface. Center still unrecrystallized.
875	8.02	37.10	303	Large grains form in center. Corners remain unrecrystallized.
875	10.05	31.57	136	Large grains form in center. Corners remain unrecrystallized.
875	14.71	23.16	...	Structure uniform.
875	29.81	15.93	...	Fine grain.
850	0.70	18.57	...	Unrecrystallized.
850	1.74	21.26	...	Unrecrystallized.
850	2.98	18.96	68	Large grains appear near surface.
850	4.15	19.31	134	Large grains on surface and sides
850	5.99	18.11	...	Large grains on surface and sides.
850	8.02	40.31	107	Large grains form in center.
850	10.05	35.28	140	Uniform recrystallization structure.
850	14.71	21.38	...	Fairly uniform.
850	29.81	12.76	...	Fine grain.
825	0.70	21.09	...	Unrecrystallized.
825	1.74	25.75	...	Unrecrystallized.
825	2.98	27.31	...	Unrecrystallized.
825	4.15	22.56	...	Unrecrystallized.
825	5.99	25.38	...	Large grains appear on surface and sides.
825	8.02	83.80	428	Large grains on whole section except in corners.
825	10.05	49.07	140	Large grains on whole section except in corners.
825	14.71	24.08	...	Complete recrystallization.
825	29.81	13.01	...	Fine grains.
800	0.70	23.82	...	Unrecrystallized.
800	1.74	19.26	...	Unrecrystallized.
800	2.98	25.51	...	Unrecrystallized.
800	4.15	17.64	...	Unrecrystallized.
800	5.99	23.09	...	Unrecrystallized.
800	8.02	23.41	...	Slightly larger grains in surface.
800	10.05	33.93	110	Large and small grains formed except in corners of section.
800	14.71	18.21	...	Fairly uniform structure.
800	29.81	9.53	...	Small grain size.
780	0.70	22.10	...	Unrecrystallized.
780	1.74	17.49	...	Unrecrystallized.
780	2.98	24.52	...	Unrecrystallized.
780	4.15	19.62	...	Unrecrystallized.
780	5.99	22.04	...	Unrecrystallized.
780	8.02	20.82	...	Unrecrystallized.
780	10.05	22.43	...	Slightly larger grain size.
780	14.71	15.64	...	
780	29.81	8.61	...	
760	0.70	.....	...	
760	1.74	20.37	...	Unrecrystallized.
760	2.98	19.46	...	Unrecrystallized.
760	4.15	.....	...	
760	5.99	19.28	...	
760	8.02	.....	...	
760	10.05	17.09	...	Possibly a slight grain size increase.
760	14.71	.....	...	
760	29.81	6.37	...	

Critical Percentages of Deformation as Judged from the Data from Table IV

Annealing Temperature	Critical Reduction for Surface Grains	Critical Reduction for Center of Section
875	2.98	5.99– 8.02
850	2.98	5.99– 8.02
825	4.15–5.99	5.99– 8.02
800	8.02	8.02–10.05
780	10.05	10.05
760	10.05	10.05–14.71

creased, the structure becomes more and more uniform over the whole section. This series of transitions is illustrated in Fig. 8 by a series of macrographs for the samples of series A.

The observed phenomena are easily attributed to nonuniformity of deformation in the rolling process. In spite of this nonuniform

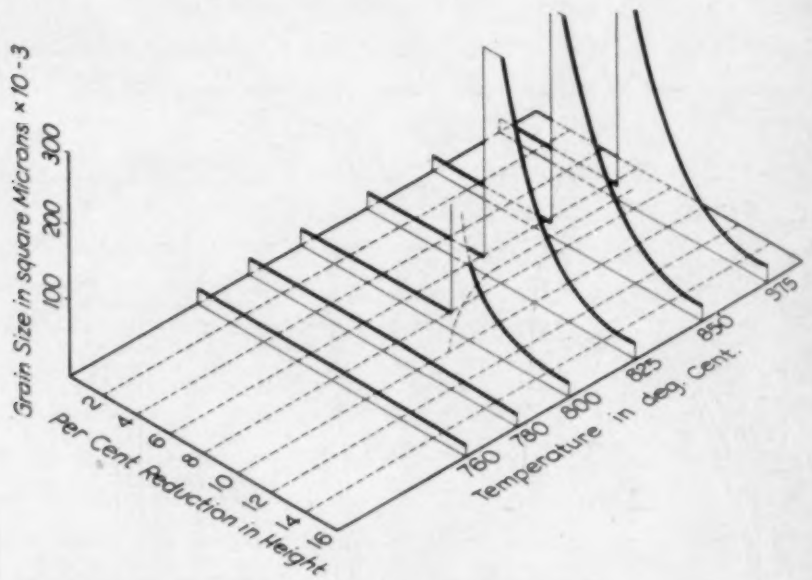


Fig. 7—Recrystallization Diagram for Armco Iron as Determined by Studies on Rolled Bars.

structure it is possible to follow the practice of past workers on recrystallization and limit consideration to the center region of the cross section. The grain size curves accompanying this report have been obtained from the grain size values obtained for the center of the section. It was found that, as was found in the work on tension-strained material, the relatively large grains formed for a critical per cent reduction were often accompanied by minute grains in the grain boundaries which, when an accurate grain count was taken, would bring the grain size down to a value giving no hint of the size of the largest grains produced. Accordingly, at those deformations at which

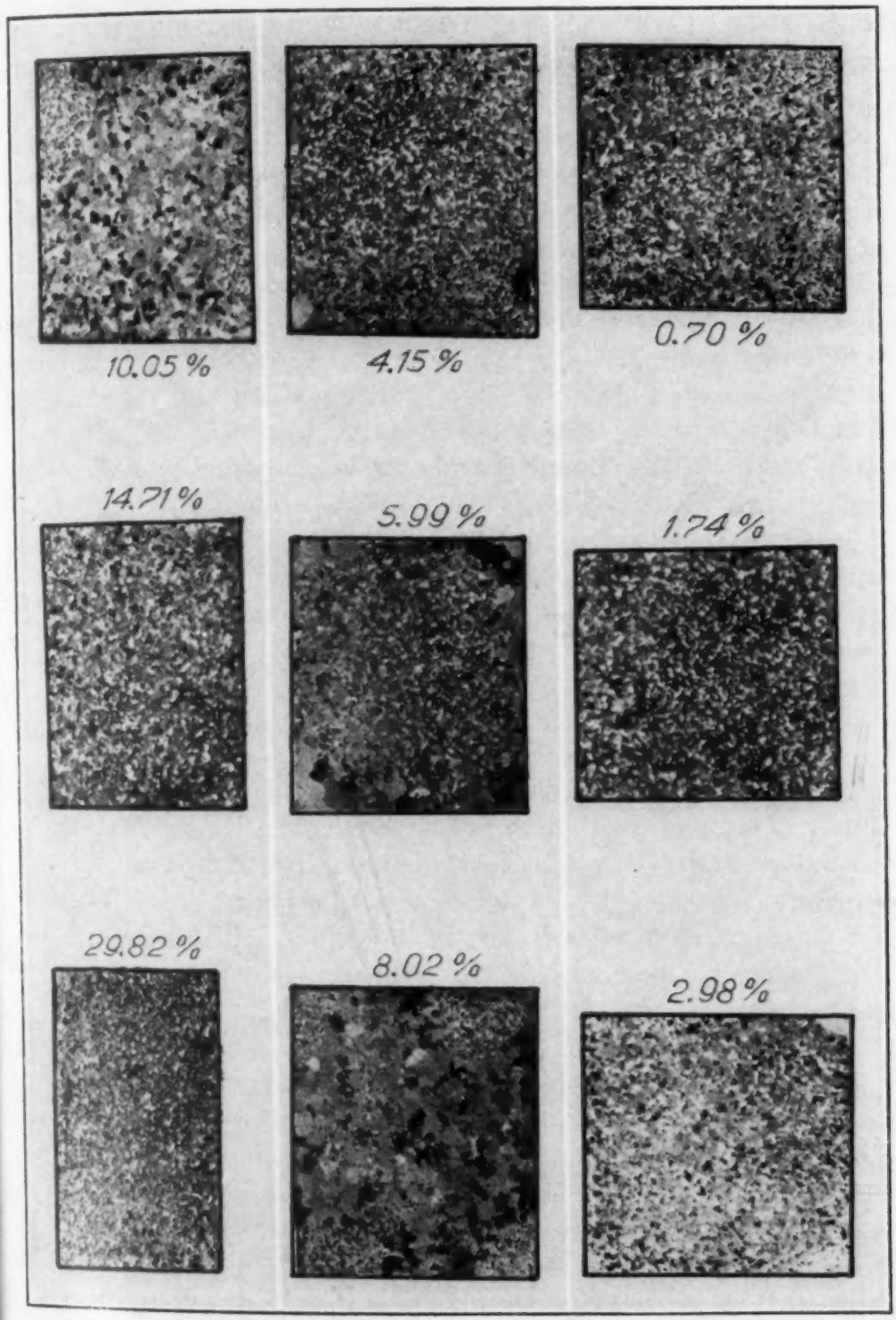


Fig. 8—Macrographs of Rolling Bar Specimens Rolled Amounts Indicated and Annealed at 875 Degrees Cent., 3 Hours.

relatively large grains appeared, the values of the sizes of the largest grains, determined from planimetry of tracings, were used to modify the grain size curve. In plotting the space diagram these modified grain size curves were used, to conform with the practice adopted in plotting the results of the tension-straining and annealing work.

The critical percentages of reduction necessary for the formation of large grains at the center of the section and also near the surface of the specimen have been tabulated. Of course these cannot be stated exactly because the critical reduction generally would occur between two values used in the experiment. These limiting values are therefore used in the table. It will be noted in this table that the critical deformations corresponding to the metal near the surface are much less in value and more sharply defined than those corresponding to the center of the section. Those for the center of the section are considerably higher than the values reported in the work on both tension and torsion-strained Armco iron. A very similar result was obtained, however, in some experiments on the recrystallization of hammered Armco iron.

Review of Results

The primary interest of this paper is not in the grain sizes that appear in the recrystallization but rather the relationship between the amounts and kinds of cold deformation required to produce recrystallization. The grain size is dependent not only upon the deformation but also upon such other factors as impurities, initial grain size, etc. The reader may gain an insight into these various factors from some of the references given at the end of this paper.

Most of the data of this paper have been summarized in Figs. 1, 5 and 7 which are the recrystallization diagrams obtained when the kind of deformation was torsion, elongation and rolling, respectively. Figs. 2, 6 and 8 give photomacrographs which illustrate the general features of each case. These recrystallization diagrams, it must be repeated, are valid only for conditions under which the experiments were performed. One of these is that the time of annealing was shown of moderate length so that the subsequent effects of grain growth were minimized. The effect of time of annealing will be mentioned again.

In the diagrams of Figs. 1, 5 and 7, there may be seen a curve in the base plane of the diagram which gives approximately the

critical deformation or that minimum degree of deformation required to bring about recrystallization at any given annealing temperature. In general these curves show that the higher the degree of deformation, the lower the temperature required to produce recrystallization. It must be mentioned, however, that toward the lower annealing temperatures, these critical deformations are more and more poorly defined, so that only at the higher temperatures can we look upon the critical deformation as a quantity capable of being determined even roughly. It would be more correct to regard the critical deformation versus temperature curve here discussed as the center of gravity of a zone or range of deformations which narrows down as the temperature in question is increased.

The curves in the base of Figs. 5 and 7 are rough curves which are intended to show the practical deformation which must be exceeded in any case to bring about a large grain structure throughout the section in the cases of tensile elongation and rolling. These curves do not indicate the degree of deformation at which large crystals may start to grow here and there in the section. This must be mentioned to avoid misunderstanding in the following discussion which centers about the critical deformation required to initiate the recrystallization process in any given case.

Therefore Table V below has been compiled which lists for each of the three types of deformation studied and for each annealing temperature used, that degree of deformation which is just great enough to initiate recrystallization. In the case of torsion strain, this is taken as the critical specific shear corresponding to that radius in the cylinder bar where a zone of recrystallized grains starts. It might be argued that a slightly greater radius corresponding to the mean centers of the first ring of grains would be the more likely starting point, but as said before, we are here interested in determining the least possible degree of deformation at which recrystallization has taken place.

In the cases of tension and rolling, the critical deformation cannot be stated more closely than the intervals in the steps by which successive specimens were deformed. Therefore, in the table the critical values for tension are indicated by the ranges in which the critical deformation is judged to lie, while in rolling, the least reduction at which recrystallization took place was chosen because here the intervals were smaller, thus allowing better judgment.

It being the object of this paper to relate the recrystallization

behavior of Armco iron deformed in various ways, it is necessary to express the degree of deformation in any case in terms of a more universal unit. This desired relationship between different types of plastic strain has also been sought for in connection with strain

Table V

Correlation of Different Kinds of Critical Deformation in Terms of Specific and Octahedral Shear

A. Deformation by Torsion

Ann. temp. °C.						
T_R	760	780	800	825	850	875
Sp. shear γ	0.208	0.131 0.166	0.094 0.141 0.151	0.085	0.0584 0.050 0.061	0.584
Oct. shear γ_8	0.169	0.107 0.136	0.076 0.114 0.124	0.069	0.048 0.041 0.050	0.047
γ_8 mean	0.169	0.121	0.105	0.069	0.0463	0.047

Where more than one determination is listed for a temperature, the results are from samples from different bars. Bars from both lots I and II are represented here.

$$\gamma_8 = \left(\frac{2}{3}\right)^{1/2} \ln\left[1 + \frac{\gamma^2}{2} + \gamma\left(1 + \frac{\gamma^2}{4}\right)^{1/2}\right]$$

B. Deformation by Elongation in Tension

T_R	700	760	780	825	875
$q = \frac{\Delta l}{l_o}$	> 0.1593	0.0783 0.0863	0.0614 0.0783	0.0346 0.0472	0.0346 0.0472
γ [$= -2 \ln (1-q)$]	> 0.3420	0.160 0.178	0.123 0.160	0.0704 0.0965	0.0704 0.0965
γ_8	> 0.210	0.104 0.115	0.0820 0.115	0.0470 0.0640	0.0470 0.064
γ_8 mean	> 0.210	0.110	0.098	0.056	0.056

$\gamma_8 = \sqrt{2} \ln (1 + q)$

C. Deformation by Rolling

T_R	760	780	800	825	850	875
$q = \frac{\Delta h}{h_o}$	> 0.100	0.100	0.080	0.0599	0.0298	0.0298
γ [$-2 \ln (1-q)$]	> 0.210	0.210	0.167	0.124	0.060	0.060
γ_8	> 0.135	0.135	0.108	0.0823	0.0417	0.0417
γ_8^*	> 0.172	0.172	0.136	0.101	0.049	0.049

$(\gamma_8^*) = -2\left(\frac{2}{3}\right)^{1/2} \ln (1-q)$ Case of pure shear as in rolling wide plate.

hardening brought about when metals are cold-deformed in different ways. Sachs[1] has considered this subject and concluded that the hardening in any type of deformation was determined by the magnitude of the deformation measured in the direction of the greatest amount of deformation and furthermore that if q is the greatest

[1]Mechanische Technologie der Metalle, Leipzig, 1925, p. 54-62.

specific elongation or reduction, it is related to the specific shear γ by the relation:

$$q = 1 - \epsilon^{-\gamma/2}$$

when γ is small (< 0.1), this is approximated by $q = \gamma/2$.

The values of γ corresponding to q have been computed in the case of elongation and rolling and entered in Table IV. If the averages of these are plotted against the corresponding annealing tem-

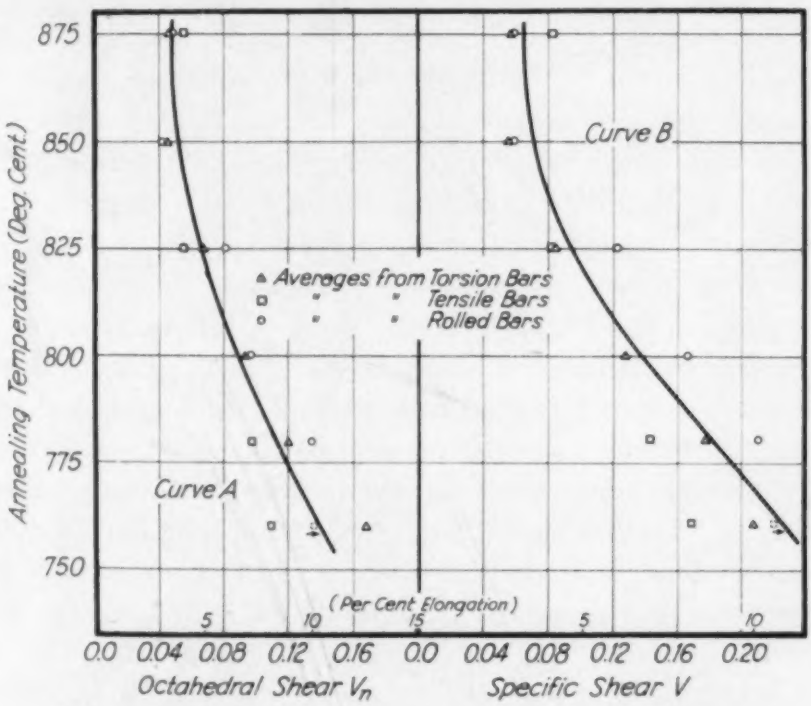


Fig. 9—Curves Showing Relation of Critical Degree of Deformation to Annealing Temperature (A) When Critical Deformation is Expressed as Octahedral Shear; and (B) When Expressed as Specific Shear.

perature as is done in Fig. 9(B), it will be seen that there is fair agreement in the case of torsion and elongation but the points for rolling are definitely out at temperatures of 825 degrees Cent. (1515 degrees Fahr.) and less.

Nadai[2] has set up a mathematical theory of plastic strain by which plastic strains of finite magnitude may be expressed solely in terms of a pure shear termed the octahedral shear. He has given formulae by which the octahedral shear may be computed from the specific shear or the principal specific extensions or contractions.

[2]Nadai, "Plastic Behavior of Metals in the Strain Hardening Range," I, *Journal of Applied Physics*, Vol. 8, March 1937, p. 205-217.

The formula for each case is given in Table V, together with the values of the octahedral shear (γ_n) computed from the data. When the mean octahedral shear values are plotted against their corresponding annealing temperatures we obtain the graph of Fig. 9(A) which is more satisfying than the one of Fig. 9(B) obtained by using the specific shear as the abscissae unit.

In Table V, part C, may be noted some values of octahedral shear (γ_n^*) which are obtained from the formula for the case of pure shear which is about the state of strain found when rolling wide sheets. As may be expected, these values do not agree with the other data because in this work the rolling was carried out in narrow bars in which the deformation is more like a simple compression.

When it is considered that the agreement of points plotted in Fig. 9(A) is good at the higher temperatures where the critical degree of deformation can be determined more definitely and still join at the lower temperature, the correlation between the results obtained from the three different types of cold work is satisfactory.

Furthermore, it must be remembered that the critical degree of deformation is not only related to the temperature of anneal but also to such other variables as time of anneal, chemical composition, etc. In fact, the critical degree of deformation is so decidedly dependent on the time of anneal that if it were not for the fact that in this work the annealing times used at the different temperatures were always about the same, the above correlations might not have been effected at all.

To determine just how important the time factor is, a few experiments were carried out, the results of which are illustrated in Figs. 10 and 11. The former shows the effect of changing the annealing time at 875 degrees Cent. (1605 degrees Fahr.) from 15 minutes to 3 hours. One may note an appreciable change in the critical radius and also a decided effect on the size of the grains themselves. It must be mentioned, however, that a previous experiment was made in which two annealing times were ½ hour and 3 hours and much less difference in results was noted so that it is likely that the 15-minute anneal created only a partial recrystallization, that is, as Ahrell has pointed out, the time factor is very important at the beginning of the recrystallization process.

However, this does not mean that the time factor vanishes as the time of anneal is increased indefinitely. Fig. 11 shows the effect of increasing the time of anneal from 1 hour to four days at 3

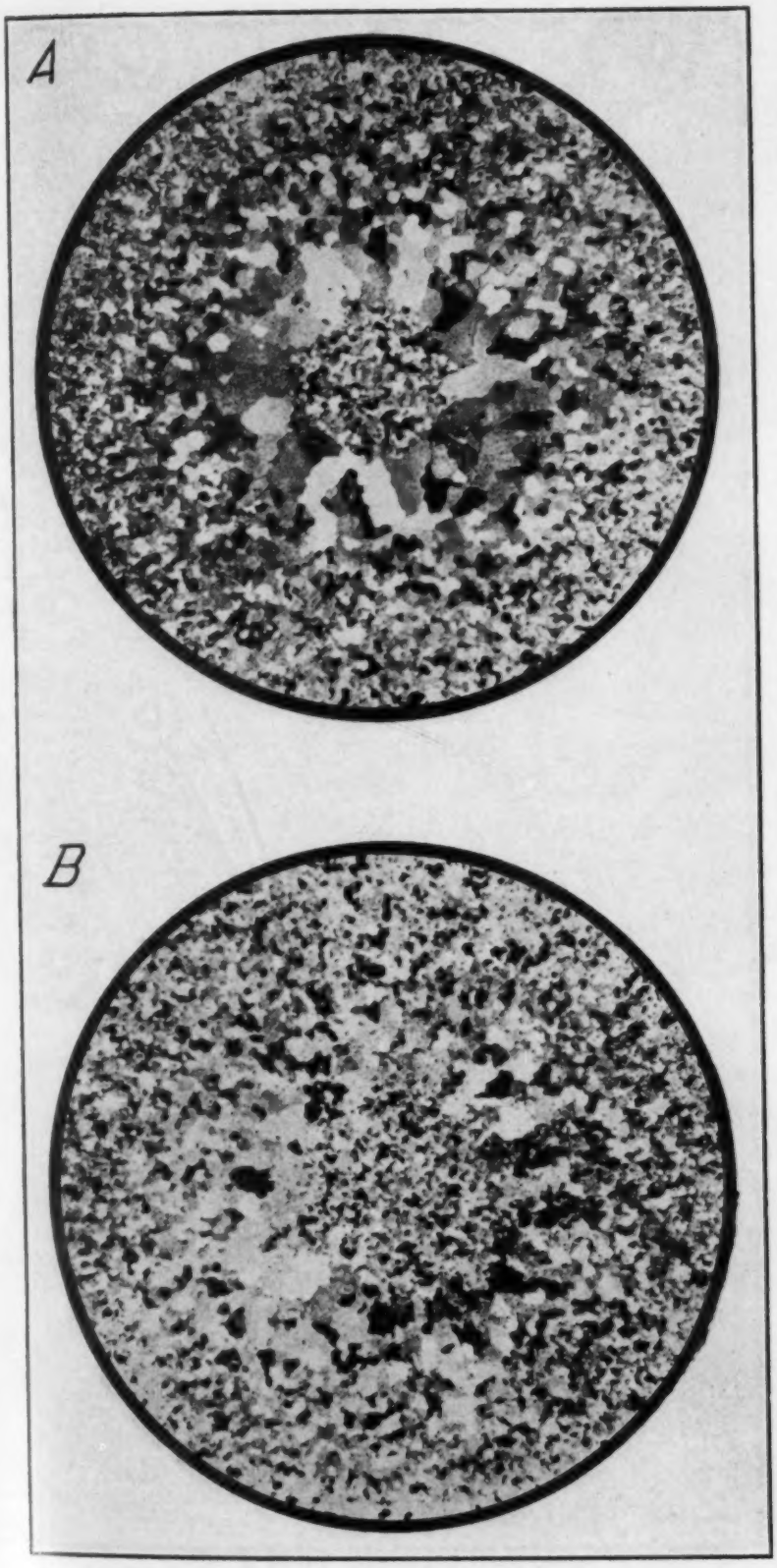


Fig. 10—Macrographs of Two Torsion-Strained Bar Samples Annealed at 875 Degrees Cent. (A) 3 Hours, (B) 15 Minutes.

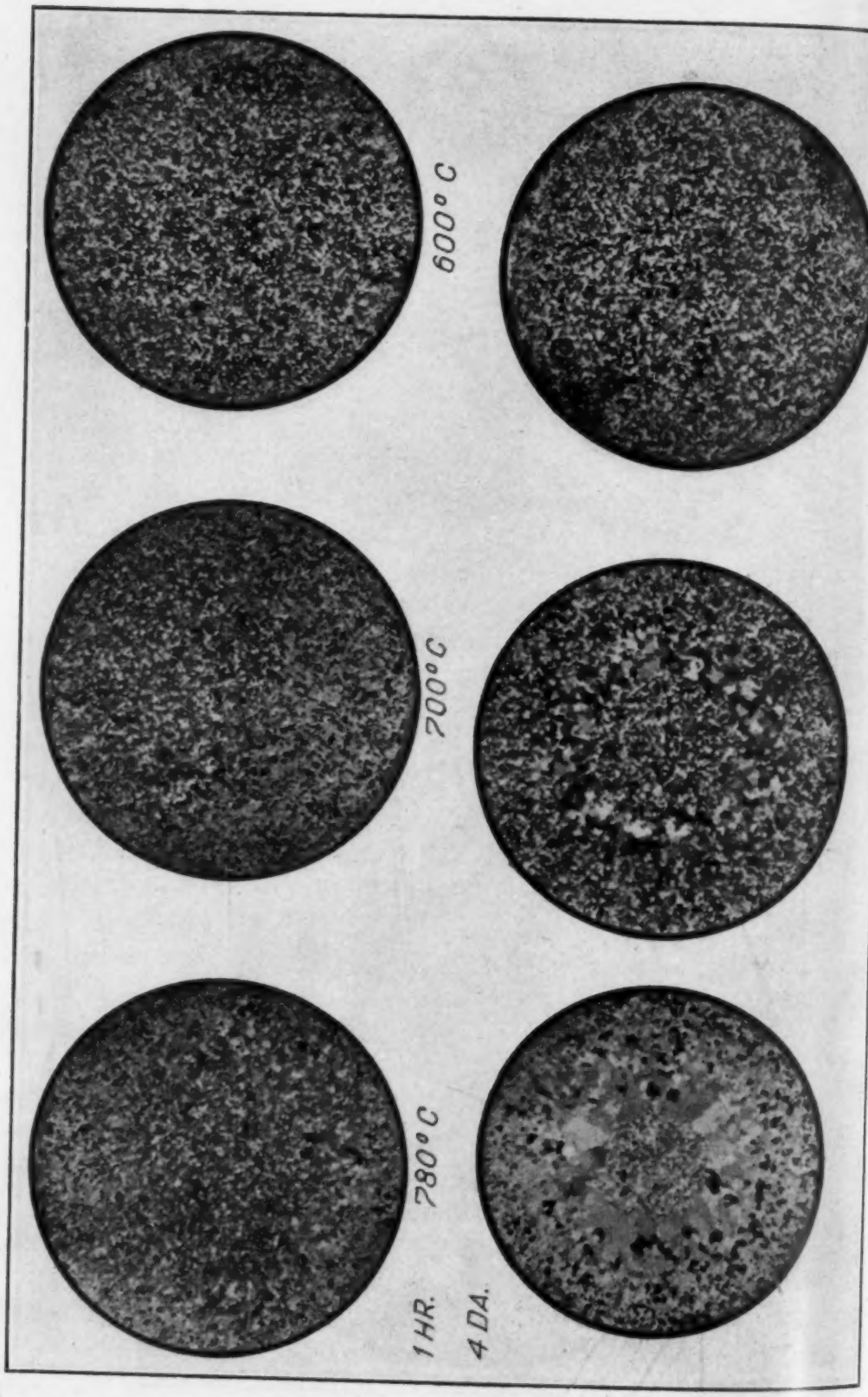


Fig. 11—Macrographs of Torsion-Strained and Annealed Samples (Bar A Lot 11) Comparing the Effect of Annealing 1 Hour and 4 Days at Each of the Temperatures 780, 700 and 600 Degrees Cent.

different annealing temperatures, all of which had little or no effect when used for only 3 hours.

While at first it may be very disconcerting to learn how decidedly the critical degree of deformation depends on the length of annealing time, this is what might be expected to hold from kinetic theory. Van Liempt has made an attempt to deduce the temperature of recrystallization theoretically by considerations similar to those used by Lindemann in his theory of melting. He derived an expression for the recrystallization temperature

$$T_R = \frac{K}{\ln 4\gamma t}$$

where K is constant or a function dependent on factors other than time, such as degree of deformation, etc., γ the characteristic frequency, and t the time of anneal. This equation bears out the experimental observation that either the critical degree of deformation or the recrystallization temperature will depend upon the time of anneal.

In this connection it is necessary to point out the need for more precise use of the term recrystallization temperature. At present it is being used indiscriminately for a number of purposes. For example, by it some authors mean the temperature at which a work hardened metal will regain its original hardness, irrespective of whether or not a change in grain structure has taken place; others again use it in place of a temperature metallurgists call the equicohesive temperature; while still others look upon it as a fundamental characteristic temperature of the metal. This last impression arises from the fact that at higher degrees of deformation the recrystallization temperature changes but little with increasing deformation.

It was the hope of early workers to relate the structural changes in recrystallization to the changes in hardness brought about, but in general it was found that those changes in the microstructure characterizing recrystallization usually occurred at temperatures quite above the highest annealing temperature required to remove the effects of work hardening. The hoped for relation between hardening and recrystallization received an additional set-back by the novel experiment of Beck and Polyani[3] who showed that an aluminum single crystal when bent increased in hardness and when straightened gained still more in hardness, but showed less tendency to recrystallize on annealing as compared to a piece that had only been bent. Similar effects

[3] *Die Naturwissenschaften*, Vol. 19, 1931, p. 505-6.

Fig. 11—Macrographs of Torsion-Strained and Annealed Samples (Bar A Lot 11) Comparing the Effect of Annealing 1 Hour and 4 Days at Each of the Temperatures 780, 700 and 600 Degrees Cent.

were observed in polycrystalline A_1 by van Arkel and van Bruggen.[4] In the present work on Armco iron attempts were made to relate the changes in hardness to the changes in structure produced by recrystallization. Since no obvious relationship could be found these results have been omitted from this paper.

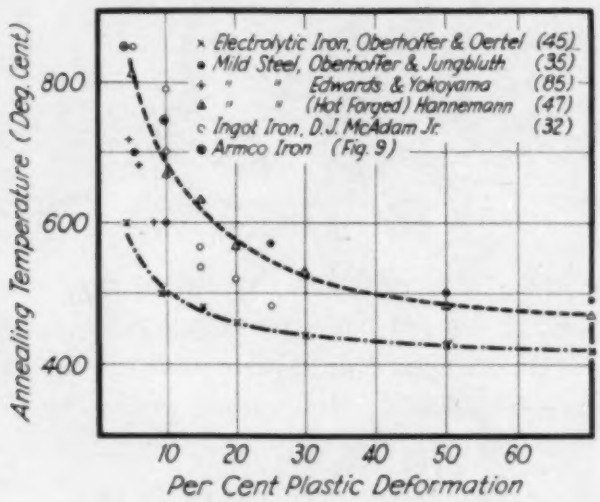


Fig. 12—Plot of Existing Data in Literature on Relation of Recrystallization Temperature to Degree of Plastic Deformation for Iron and Mild Steels.

Fig. 12 shows plotted on a single sheet the available data in the literature on the relation of critical degree of deformation to annealing or recrystallization temperature for pure iron and mild steels. The considerable variation in these curves obtained by different workers indicates the importance of the effect of impurities on the recrystallization process. That all of the data could be grouped about a mean curve suggests that there is a fundamental relationship between critical degree of deformation and annealing temperature characteristic of the metal itself. To compare the results obtained in this work with these data, points from this work are included in the figure. It may be noted that these agree somewhat with values taken from data by D. J. McAdam (32) for American ingot iron and also quite oddly with values determined by Hanemann (47) in hot deformation (deformation carried out at anneal temperature) for mild steels. In general, the recrystallization temperature of Armco iron and mild steels is definitely higher than for electrolytic iron.

In conclusion, it must be repeated that the phenomena of recrystallization are complex and that much experimental work directed

[4] *Z. Physik*, Vol. 80, 1933, p. 763-791.

at particular factors, keeping other factors as alike as possible, must yet be carried out to get our knowledge of these phenomena on a more rational basis.

Summary

1. The recrystallization of Armco iron when cold-deformed and annealed has been studied for the cases in which the cold deformation consisted of torsion, elongation in tension, and rolling. The results have been summarized in recrystallization diagrams.

2. By expressing the degree of deformation in each type of cold work in terms of the corresponding octahedral shear, the critical degree of deformation so expressed is the same for the three kinds of cold work studied. Therefore, by means of recrystallization studies in torsionally-strained bars, it is possible to establish the most important part of the recrystallization diagram (small deformations—high temperature) with attendant simplification of technique.

3. Studies on the effect of annealing time have shown that as has been anticipated by theory, the critical degree of reduction decreases as the length of annealing time is increased.

Acknowledgments

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DISCUSSION

Written Discussion: By H. S. Rawdon, chief, Division of Metallurgy, National Bureau of Standards, Washington, D. C.

The ordinary reader of a paper of this kind falls very far short in his appreciation of the very great number of data which must be acquired in order to establish any generalization in a field of this kind. Each of the 3-dimension graphs summarizes a host of test data. The authors are to be especially commended for the excellence of their presentation of a subject which might easily have been obscured by the inclusion of many unessential details.

A very distinct service has been rendered to metallography and particularly to workers interested in the subject of recrystallization of cold-worked metals by the establishment of the fact that the mode of deformation is unimportant in studies of this kind. The torsional method is far simpler to operate than other deformation methods and future workers in this field can use this method with a feeling of security now that it has been shown that the results are identical with those obtained by other straining methods.

Although this study has been confined to a single material, "Armco iron," it is believed that the general conclusions reached are applicable to the class

of materials represented, that is, "open-hearth iron," and are not to be restricted, as the title might indicate, to the special material used. The advisability of designating materials in technical reports by trade names may very properly be questioned. Provided the nature of the material and its source are clearly set forth, further reference to the material might well be couched in more general terms, i.e., the class of material of which this is a specific example.

The writer was especially interested in the unusual phenomenon described by Beck and Polyani (referred to on page 255) that a single-crystal metal specimen, after being deformed and hardened by single bending, recrystallized upon annealing, as would be expected, but a similar specimen bent and restraightened did not recrystallize on annealing. In order to satisfy his curiosity, as to what metal was used, the writer consulted the original account. The metal was aluminum but, by a typographical error in the text, this is described as "an A_1 single crystal." For others who may be interested in the original report, it may also be mentioned that the journal is "Die Naturwissenschaften," not "Nature," as given in the convention preprint.

Written Discussion: By H. E. Publow, head, department chemical engineering, Michigan State College, East Lansing, Mich.

I would like to congratulate the authors, Messrs. Kaiser and Taylor, on their excellent paper. They have contributed much to our knowledge of the effect of cold working on the grain structure of Armco iron. There is only one point that I would like to discuss, the words recrystallization and grain formation. Apparently these two terms are used synonymously, thus considering that a crystal of iron and a grain of iron are the same thing. I do not believe that a crystal is necessarily a grain, although a grain may consist of a single crystal. May there not be cases when a grain consists of many crystals? A crystal should have a definite internal atomic or molecular structure. The mere fact that a certain etchant gives us a microscopic pattern, I do not think justifies the assumption that this pattern shows necessarily individual crystals. An alloy cannot be considered as a mixture of crystalline aggregates, each having its own individuality; rather the same etched pattern is characteristic of the same type only of alloy. Take for instance our normal pearlite, supposedly a mixture of ferrite and cementite, this fact being determined by visual observation. Yet when the critical temperature is reached on heating we say that the ferrite and cementite dissolve in one another to produce a solid solution. If either ferrite or cementite were heated alone they would not transform at the same temperatures as they do when combined in the form of pearlite. Does not this mean then that there are other forces and conditions existing in the alloy than is apparent from their grain structure, and that the terms recrystallization and regranulation may not be the same thing? If a specimen of very low carbon steel is pressed in a die distorted and reduced in cross section, if it has not been worked too severely, it will not show any distortion of the grains. It does not seem possible that one grain can move past another, consequently I do not believe that the pattern which we produce on etching a metal is necessarily the true crystal structure but rather a combined physical and chemical phenomenon which for similar types of metal shows characteristic patterns.

Written Discussion: By A. Nadai, consulting mechanical engineer, Research Laboratories, Westinghouse Electric & Manufacturing Co., E. Pittsburgh, Pa.

These attempts of the authors to correlate the grain size after recrystallization with the cold deformation by straining steel in various ways, by tension, by torsion or through rolling, deserve further attention. Although the recrystallization laws have been investigated by many workers the authors are among the first ones who have more thoroughly compared the effects of different types of strain on the redistribution of the grains.

In investigations of a metallurgical nature of this kind an important question of a mechanical nature is hidden. The question must immediately arise whether a simple quantity dependent solely on the state of strain exists, which could be considered as a measure of the various degrees of plastic deformations. The question is by no means simple or an easy one to answer. Under certain conditions when certain precautions have been taken during the preparation of samples for tests, a polycrystalline metal can be considered as an isotropic material. For practical purposes one can assume that it has no pronounced directional differences in its mechanical properties in the unstrained state.

Experiments have shown that this may be true even after the metal has been deformed plastically, provided the permanent strains have not been too large. In other words, the further assumption is made that a polycrystalline metal after it has undergone plastic deformation is still essentially an isotropic material. The shearing strain γ_n which depends on the three principal strains can under these conditions serve as a measure of the cold deformation, provided that the temperatures under which the plastic deformations were produced are sufficiently low, so that the effect of another important group of variables, namely, that of the strain rates, has not yet become appreciable. With the increasing plastic strains, however, conditions certainly will become more involved. The fibrous structures found in wires after much cold drawing or the preferred lattice orientation in the elongated crystallites after considerable cold rolling and other known phenomena to be observed in the structure of metals after considerable deformation seem to indicate that with increasing plastic deformations mechanical isotropy is lost gradually—large amounts of cold work applied to an originally isotropic metal gradually change it into an anisotropic material, in which the mechanical properties (both the elastic and the plastic ones) depend on the direction in which one investigates them. It deserves to be commended that the authors have confined their work to the former range of strains and by restricting the amounts of cold deformation to smaller orders of magnitude, were able to find a good agreement between the grain size after recrystallization and the previous cold deformation.

M. F. JUDKINS:[6] I should like to ask as a matter of personal interest about the effect of hardness upon the rate of recrystallization which would seem to be related to viscosity or rigidity which is in turn proportional to hardness. I should like to ask if hardness determinations of the resultant strain hardening consequent upon the cold working were obtained? The increase in hardness was not appreciable owing to the absence of alloying elements.

Authors' Reply

The experimental conditions in this work were such that there is reason to feel that the equations derived by Dr. Nadai should be valid. The deformations were carried out at room temperature and in the cases of torsion and tensile elongation the rates of deformation were low. In the rolling they were moderately so. Thus the conditions favor the absence of the strain rate effects that Dr. Nadai mentions. Next, granting that the results of these experiments show that a definite state of strain characterized by the octahedral shear is necessary to initiate the recrystallization process upon annealing at some specified temperature, there is still lacking a physical interpretation of this fact. There remains the task of drawing a physical picture of what happens when a given crystal in this critical state of strain grows, upon heating to an elevated temperature, into a new crystal. The fact that the critical strain is dependent on the time of anneal and other variables makes the problem even more complex than ever. It is likely that atomic theories of recrystallization and plasticity such as proposed by Dehlinger and others will eventually give an insight into the actual mechanism of recrystallization.

We share with Dr. Rawdon the wish that the results obtained with this particular metal Armco iron may apply to other single phase metals, but extrapolating from what is known to what is unknown is always uncertain. It is known, however, from the literature on the recrystallization of single phase metals that their recrystallization behaviors are strikingly similar so that it is quite likely that we should find a similar relation in other metals between degree of cold work expressed in its simplest possible unit and the recrystallization temperature. We thank Dr. Rawdon for calling attention to the error in print and in the quoted reference on the bending and recrystallization of aluminum single crystals.

Dr. Publow's remarks indicate the need for a concise terminology in describing recrystallization phenomena. Whether or not a grain is truly a crystal depends in the last analysis on whether X-rays will show that all the atoms within it are aligned in a single perfect or nearly perfect geometrical array. This definition of a crystal can perhaps be made so strict that no real grain can satisfy it due to its natural imperfections. In general in heat treated iron the nature of the etch pits on a section is such that we can feel fairly sure that we are dealing with crystals. The word "grain" has been used in this paper to designate the individuals in the microsection and at times includes both strained and unstrained metal. Its meaning is thus more general than the word "crystal."

Mr. Judkins' questions on the hardness conditions existing in the specimens are interesting, but as mentioned before no obvious relationship could be found between the hardness gradient existing in the cold-worked torsion specimens to the grain structures appearing upon annealing. Rockwell hardnesses were measured in the cold-worked torsion samples at a number of radii and it was found that the hardness increased continuously with the radius or shear. The grain size curves for the same samples annealed usually show no increase in

[5]Chief engineer, Firthite division, Firth-Sterling Steel Co., McKeesport, Pa.

grain size up to some critical radius, and then a very abrupt and tremendous increase in the grain size. After annealing, the hardness usually showed a continuous decrease from the center to the outside. This seems to be another example of the observation that the relief of strain hardening on annealing and the true recrystallization process are distinct processes, the latter process usually, but not necessarily always, occurring at temperatures considerably higher than those for the former.

SOME EFFECTS OF DEOXIDIZERS IN LOW CARBON-1.5 PER CENT CHROMIUM STEEL

By Walter Crafts and John L. Lamont

Abstract

In order to determine the reasons for differences between the properties of similar fine-grained steels, the "core" properties of 1.5 per cent chromium carburizing steels treated with graduated amounts of aluminum, vanadium, and zirconium have been investigated. Using the tensile strength and the distortion of a tuning fork type of specimen as criteria of hardening characteristics, it has been shown that the differences in properties result from changes in the mode of transformation of austenite. The amount and kind of deoxidizer have been found not only to have an appreciable influence over the austenite transformation in one section, but also to determine the differences between light and heavier sections. More accurate control and more desirable combinations of properties have, therefore, been shown to be obtainable by accurate control of the residual deoxidizer content and the use of combinations of deoxidizing elements.

SINCE the recognition of the advantages and subsequent widespread use of fine-grained steels, several anomalies in the properties of steels of comparable grain size have been observed. In steels made fine-grained with aluminum, the differences between "normal" and "abnormal" steels were described by McQuaid and Ehn (1)[1] in 1922. More recently McQuaid (2) pointed out similar differences of a smaller order of magnitude in the fine-grained steels that Jominy and Boegehold (2) found to be of variable hardenability. That aluminum-treated steels with different inherent grain size do not transform at the same rate when heat treated to the same actual grain size was demonstrated by Herty (3) who found a higher reaction rate in steels that had a finer inherent grain size. Similarly Zimmerman, Aborn, and Bain (4) have shown relatively greater hardenability

[1]The figures appearing in parentheses pertain to the references appended to this paper.

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for a given grain size in vanadium steel. Observations of this type have led to the opinion that although both actual and inherent grain size have a major influence, certain other factors have a significant effect on the hardening characteristics.

Variable properties were found in chromium carburizing steels that are characteristically normal (5) and the problem was investigated by tests on 0.10 per cent carbon, 1.5 per cent chromium steels containing graduated amounts of the grain-refining elements, aluminum, vanadium, and zirconium. The tests were limited to un-

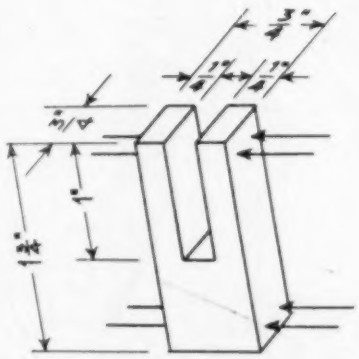


Fig. 1—Tuning Fork Distortion Specimen.

carburized specimens, except to determine McQuaid-Ehn grain size, and the tensile strength and distortion of the "core" material have been used as the primary criteria of hardenability. A limited study has also been made to illustrate the combinations of properties that may be produced by treatment with more than one deoxidizer.

Procedure

The steels, shown in Table I, were made at the Union Carbide and Carbon Research Laboratories, in small, basic, high frequency furnaces and forged under uniform conditions. The bars were first given a normalized treatment at 925 degrees Cent. (1700 degrees Fahr.). Tensile and Izod impact specimens in the form of 7/8-inch diameter bars were heated to 925 degrees Cent. (1700 degrees Fahr.). held for one hour, oil-quenched and tempered at 150 degrees Cent. for one hour. Distortion specimens of a type similar to that used by McMullan (6), as shown in Fig. 1, were carefully measured at the points indicated by the large arrows, heated in a nitrogen atmos-

phere at 925 degrees Cent. (1700 degrees Fahr.) for 1 hour, oil-quenched, and remeasured both at the base and across the ends of the prongs. The amount of contraction or expansion of the prongs has been called "distortion" in the following discussion.

Table I
Chemical Analyses

Steel No.	% C*	% Mn	% Si	% Cr	% Al*	% Al_2O_3*	% V	% Zr*	% ZrO_2*
1-Al	0.140	0.33	0.20	1.50	0.007	0.006	....	....	....
2-Al	0.132	0.36	0.22	1.50	0.010	0.016	....	....	....
3-Al	0.115	0.34	0.24	1.49	0.012	0.015	....	....	....
4-Al	0.120	0.34	0.22	1.51	0.018	0.012	....	....	....
5-Al	0.105	0.35	0.22	1.52	0.020	0.010	....	....	....
6-Al	0.114	0.41	0.27	1.52	0.024	0.013	....	....	....
7-Al	0.130	0.36	0.23	1.49	0.029	0.019	....	....	....
8-Al	0.121	0.33	0.23	1.50	0.066	0.015	....	....	....
1-V	0.105	0.34	0.27	1.50	....	....	0.029	....	....
2-V	0.101	0.33	0.20	1.50	....	....	0.049	....	....
3-V	0.115	0.30	0.17	1.53	....	....	0.113	....	....
4-V	0.097	0.36	0.23	1.47	....	....	0.160	....	....
5-V	0.113	0.35	0.28	1.43	....	....	0.216	....	....
6-V	0.108	0.36	0.28	1.50	....	....	0.245	....	....
1-Zr	0.107	0.33	0.26	1.49	....	....	....	0.005	0.040
2-Zr	0.101	0.32	0.22	1.52	....	....	....	0.007	0.059
3-Zr	0.120	0.38	0.33	1.48	....	....	....	0.015	0.071
4-Zr	0.144	0.30	0.31	1.51	....	....	....	0.031	0.073
5-Zr	0.112	0.33	0.34	1.46	....	....	....	0.063	0.096

*Average of several determinations.

The mode of transformation of austenite during quenching was also determined. Specimens ½ and $\frac{13}{16}$ inch in diameter by 2 inches long, corresponding approximately to the cross sections of the prong and base of the distortion specimen as well as the section of the heat treated tensile and impact specimens, were quenched in a dilatometer similar to that used by Bain and Waring (7). Time was measured by the second hand of a clock, changes of length were determined with a dial indicator and temperature was indicated by a platinum thermocouple connected with a millivoltmeter. Observations of length, temperature, and time were made by photographing the dials with a moving picture camera. The absolute accuracy of the measurements, particularly that of the temperature, is considered to be rather low, but the relative accuracy was of an adequately high order. The intervals of discontinuity in the contraction were considered to be the most reliable measurements, and have been used to illustrate the amounts of ferrite, pseudomartensite, and martensite formed during transformation.

In chemical analysis of the amounts of aluminum and zirconium present in the steels, both the total amount present and the amount that was insoluble in 10 per cent sulphuric acid were determined. The acid-insoluble material was considered to represent inclusions of appreciable size, such as might be observed under the microscope.

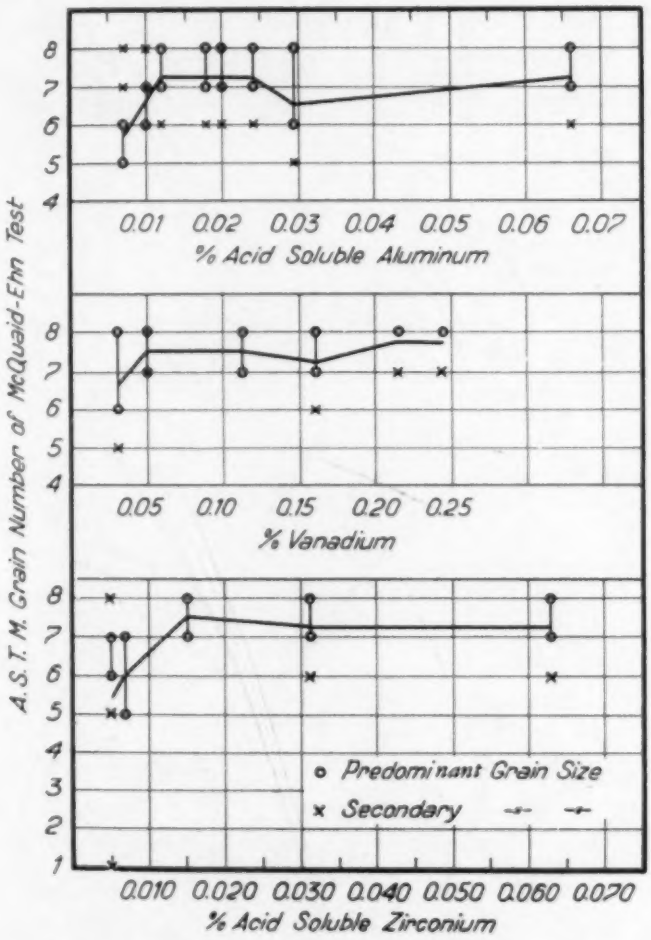


Fig. 2—Effect of Acid Soluble Deoxidizers on Grain Size.

It is called "oxide" in Table I, although the residue was not analyzed to determine the composition. The difference between the total and the insoluble amounts was designated as the "acid-soluble" aluminum or zirconium content. Since the acid-soluble deoxidizer content gave the best correlation with other properties, it has been used to indicate the effective content of deoxidizing element. It has not been established whether the acid-soluble portion of the deoxidizing element is present in the steel as alloy, soluble metallic compound or very finely divided nonmetallic compound.

McQuaid-Ehn Grain Size

The McQuaid-Ehn grain size test was carried out for 8 hours at 925 degrees Cent. (1700 degrees Fahr.) in accordance with the A.S.T.M. specification E19-33 and the results are shown in Table II.

Table II
A.S.T.M. Grain Number in McQuaid-Ehn Test

Steel No.	% Al	% Al_2O_3	Predominant Grain Size	Secondary Grain Size
1-Al	0.007	0.006	5–6	7–8
2-Al	0.010	0.016	6–7	8
3-Al	0.012	0.015	7–8	6
4-Al	0.018	0.012	7–8	6
5-Al	0.020	0.010	7–8	6
6-Al	0.024	0.013	7–8	6
7-Al	0.029	0.019	6–8	5
8-Al	0.066	0.015	7–8	6
	% V			
1-V	0.029	....	6–8	5
2-V	0.049	....	7–8	-
3-V	0.113	....	7–8	-
4-V	0.160	....	7–8	6
5-V	0.216	....	8	7
6-V	0.245	....	8	7
	% Zr	% ZrO_2		
1-Zr	0.005	0.040	6–7	1-5, 8
2-Zr	0.007	0.059	5–7	-
3-Zr	0.015	0.071	7–8	-
4-Zr	0.031	0.073	7–8	6
5-Zr	0.063	0.096	7–8	6

The grain size numbers have been plotted against acid-soluble deoxidizer content in Fig. 2. It will be noted that a small amount of residual deoxidizer (0.01 per cent aluminum, 0.05 per cent vanadium, and 0.015 per cent zirconium) was sufficient to develop substantially the fine-grained condition, and that additional amounts had no material influence on grain size. From this it would appear that above a critical amount the McQuaid-Ehn grain size is not proportional to the acid-soluble amount of the deoxidizer. There also appeared to be no relation between grain size and the larger nonmetallic forms of the deoxidizers, as indicated by the amounts of acid-insoluble deoxidizers given in Table II.

Tensile and Impact Properties

The tensile and impact properties are shown in Table III. There did not appear to be any well-defined relation between these proper-

ties and McQuaid-Ehn grain size except in the ductility and impact strength of the aluminum-treated series. In this case lower values were found in the coarser-grained steels. This was not true of the other deoxidizers in which high ductility and impact strength were found in relatively coarse-grained as well as in the fine-grained steels.

When the effect of small variations of carbon content were eliminated by suitable corrections, the relations shown in Fig. 3 were

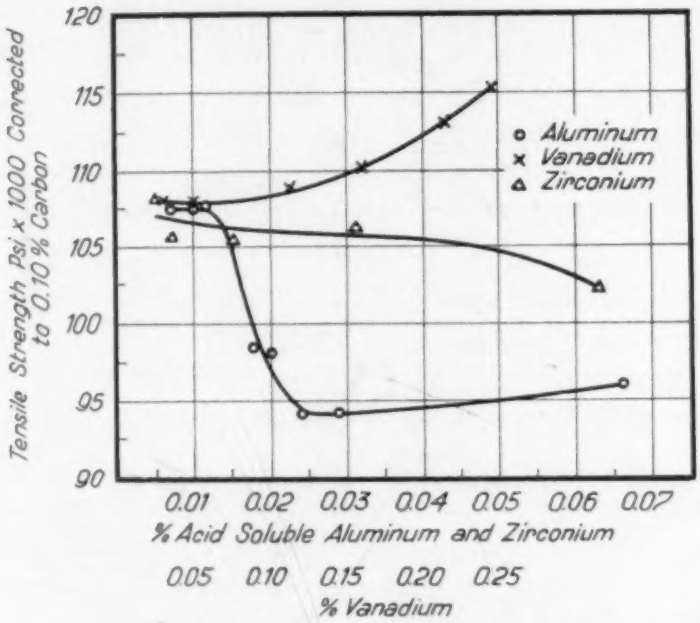


Fig. 3—Effect of Acid Soluble Deoxidizer Content on Corrected Tensile Strength.

found between corrected tensile strength and acid-soluble deoxidizer content. All of the steels containing small amounts of deoxidizers had tensile strengths closely approaching 107,500 pounds per square inch. Larger deoxidizer contents had effects that were specific to the individual element. Vanadium produced an increase of strength that was quite appreciably above 0.15 per cent. Zirconium had a slight tendency to lower the strength. In the case of aluminum the strength was unchanged up to 0.012 per cent aluminum but higher amounts produced an abrupt drop from 107,500 to 94,000 pounds per square inch at 0.025 per cent aluminum. It is notable that the drop in tensile strength occurred at a higher aluminum content than that which produced the maximum degree of grain refinement. The tensile strength was, therefore, found to be governed by the amount and kind of residual acid-soluble deoxidizer.

Table III

Mechanical Properties of Steels After Oil Quenching From 925 Degrees Cent. (1700 Degrees Fahr.) and Tempering at 150 Degrees Cent.

Steel No.	% Al	Yield Point lbs./sq. in.	Tensile Strength lbs./sq. in.	% El. in 2 in.	% R.A.	Izod Impact Ft./lb.	Tensile Strength psi—Corrected to 0.10% Carbon
1-Al	0.007	91,000	123,500	13.0	24.1	23.5	107,500
2-Al	0.010	82,000	120,500	15.5	34.4	24.3	107,700
3-Al	0.012	86,000	113,750	20.5	50.6	35.0	107,750
4-Al	0.018	53,000	106,500	20.0	46.6	39.3	98,500
5-Al	0.020	51,000	100,000	22.0	46.3	48.0	98,000
6-Al	0.024	54,000	99,700	22.5	43.8	47.0	94,100
7-Al	0.029	68,000	102,250	24.5	53.8	49.3	94,250
8-Al	0.066	68,500	104,500	24.0	53.6	44.4	96,100
	% V						
1-V	0.029	84,000	110,000	22.0	56.5	41.5	108,200
2-V	0.049	73,500	108,250	23.5	59.4	49.5	107,850
3-V	0.113	71,000	113,000	23.0	50.6	41.5	108,800
4-V	0.160	70,000	109,000	24.0	59.6	54.0	110,200
5-V	0.216	76,500	118,250	23.0	56.8	51.8	113,050
6-V	0.245	79,500	118,500	21.5	54.1	47.3	115,300
	% Zr						
1-Zr	0.005	80,000	111,000	21.0	58.8	41.0	108,200
2-Zr	0.007	74,000	106,000	22.0	56.5	45.5	105,600
3-Zr	0.015	74,500	113,500	21.0	57.0	39.0	105,500
4-Zr	0.031	74,500	114,000	22.5	56.2	33.0	106,400
5-Zr	0.063	77,000	107,000	19.0	57.0	36.0	102,200

Table IV

Distortion Values After Oil Quenching From 925 Degrees Cent. (1700 Degrees Fahr.)

Steel No.	% Al	Average Distortion Inches x 10^{-4}
1-Al	0.007	+18.5
2-Al	0.010	+10.0
3-Al	0.012	— 4.0
4-Al	0.018	— 2.0
5-Al	0.020	— 5.5
6-Al	0.024	+ 1.0
7-Al	0.029	—11.0
8-Al	0.066	—14.5
	% V	
1-V	0.029	+20.0
2-V	0.049	— 6.5
3-V	0.113	— 3.0
4-V	0.160	+ 9.5
5-V	0.216	+18.5
6-V	0.245	+24.0
	% Zr	
1-Zr	0.005	— 4.5
2-Zr	0.007	—12.0
3-Zr	0.015	— 9.0
4-Zr	0.031	—13.5
5-Zr	0.063	—10.0

The ductility was higher in the zirconium and vanadium steels than in the aluminum steels. The vanadium steels were highest in impact strength. The differences in ductility and impact strength were rather small and appeared to be characteristic of the deoxidizer. All except the coarser-grained aluminum steels were of a high order

of ductility and impact strength. No relation between the yield point and grain size or amount or kind of deoxidizer could be established.

Distortion Characteristics

Measurement across the prongs of the tuning fork specimen, before and after oil-quenching from 925 degrees Cent. (1700 degrees Fahr.), gave the differences shown in Table IV. These values have been plotted with respect to acid-soluble deoxidizer content in Fig. 4. It will be noted that there is a slight tendency for the coarser-grained steels to expand; i.e., to have a plus distortion value. The amount, however, varied widely between +0.0020 and —0.0005 inch in the coarser-grained steels. Among the fine-grained steels the aluminum- and zirconium-treated steels contracted, while the vanadium steels expanded.

The distortion, as illustrated in Fig. 4, appeared to depend on the kind and amount of deoxidizer residual in the steel. Increase of aluminum gradually changed the distortion from expansion to contraction along a curve of the hyperbolic type. Vanadium produced a similar type of curve when small amounts were present but in larger amounts caused a reversion to positive distortion. In the zirconium series all of the specimens gave negative distortion although there appeared to be a tendency toward a minimum in the neighborhood of 0.03 per cent zirconium. There is a suggestion of similarity between all of the curves, but the ranges investigated were not sufficiently broad to permit any generalization regarding a typical deoxidizer versus distortion relationship. Although there probably is such a general relationship it is apparent that the quantitative effects of the deoxidizers are very different, and that the amounts commonly used to develop grain refinement produce widely different tendencies to distortion.

In order to determine whether the amount of variation of distortion produced by different deoxidation treatment was of a significant order, similar distortion tests were made on a few commercially purchased carburizing steels. These steels gave the following amounts of distortion: S.A.E. 1015, —0.0020 inch; S.A.E. 1315, —0.0034 inch; S.A.E. 4615, +0.0050 inch; S.A.E. 6115, +0.0020 inch. All of these steels were fine-grained and appeared to have been treated with aluminum except the vanadium steel. As the distortion values on the 1.5 per cent chromium steels ranged from —0.0014 to +0.0024

inch, the spread of distortion produced by deoxidizers was about half of that produced by alloys among the steels tested. This observation has also been confirmed on other steels that are not described in this paper, and it may be concluded that the effect of grain-refining deoxidizers on distortion is nearly of the same order as that produced by the elements that are usually classed as alloying elements.

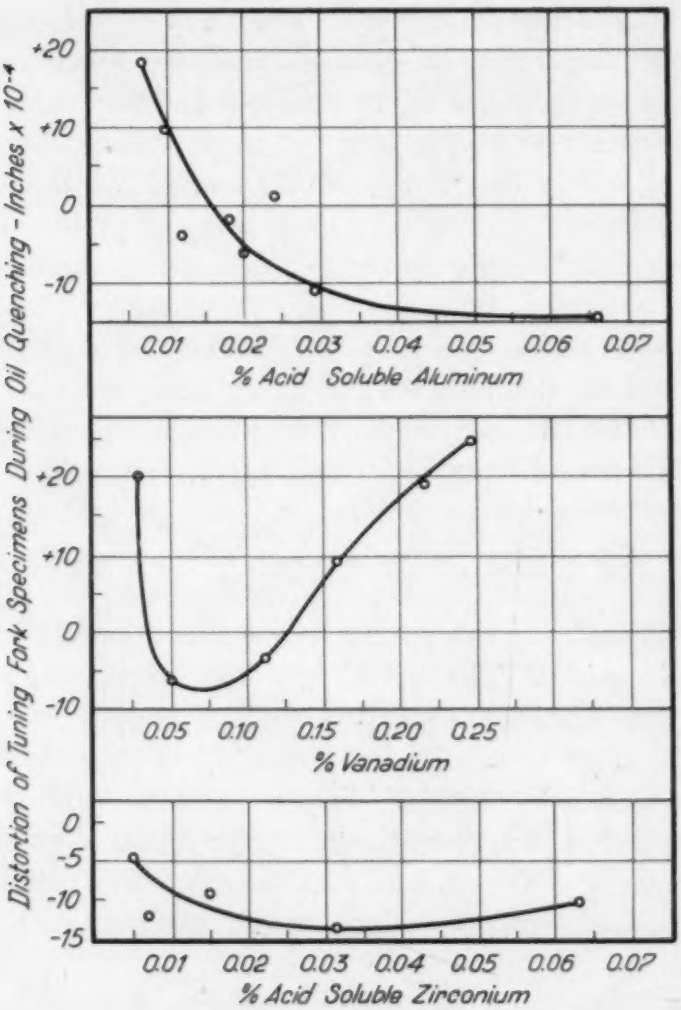


Fig. 4—Effect of Acid Soluble Deoxidizer Content on Distortion Occurring During Quenching.

Austenite Transformation During Oil-Quenching

As considerable differences of tensile strength and distortion resulted from changes in the amount and kind of deoxidizing element, an effort was made to determine whether the differences could be reduced to a common basis by determining the mechanism of the

austenite transformation. The discontinuities of temperature and contraction were therefore determined during oil quenching by the dilatometric method described above. Due to temperature gradients within the specimens, the measured temperatures and dilation intervals represent only the over-all transformation characteristics of the specimen rather than the true condition of transformation such as might be obtained on very small specimens.

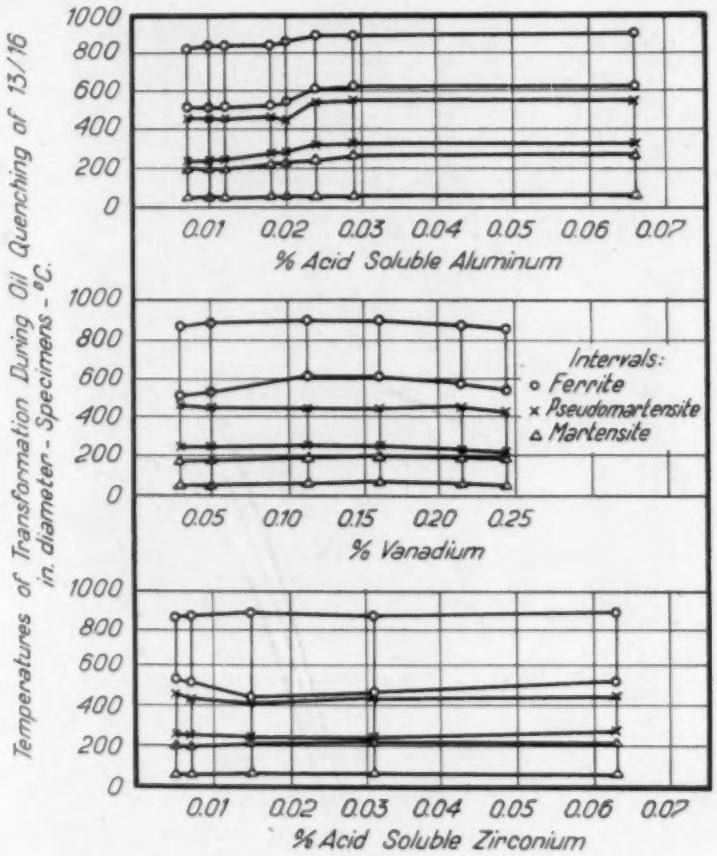


Fig. 5—Effect of Acid Soluble Deoxidizer Contents on Transformation Temperature Occurring in $\frac{13}{16}$-Inch Diameter Specimens.

The transformation was found to occur in three steps, with the formation of ferrite, pseudomartensite, and martensite. The approximate temperatures of formation may be seen in Fig. 5, and a typical structure is shown in Fig. 6. It will be seen that increase of aluminum tended to restrict the temperature range of ferrite formation, changed the pseudomartensite range little, and increased the martensite range. The temperatures of formation of all the constituents were shifted to higher temperatures by higher aluminum

contents. Intermediate amounts of vanadium restricted the ferrite range, but the other changes were quite small. Zirconium steels were characterized by the formation of ferrite over a very long range of temperature.

The lengths of the discontinuities in the contraction of the specimen during quenching, in which the expansion due to the higher specific volume of the transformed material tended to oppose the thermal contraction of cooling, are shown in Figs. 7, 9, and 10. It

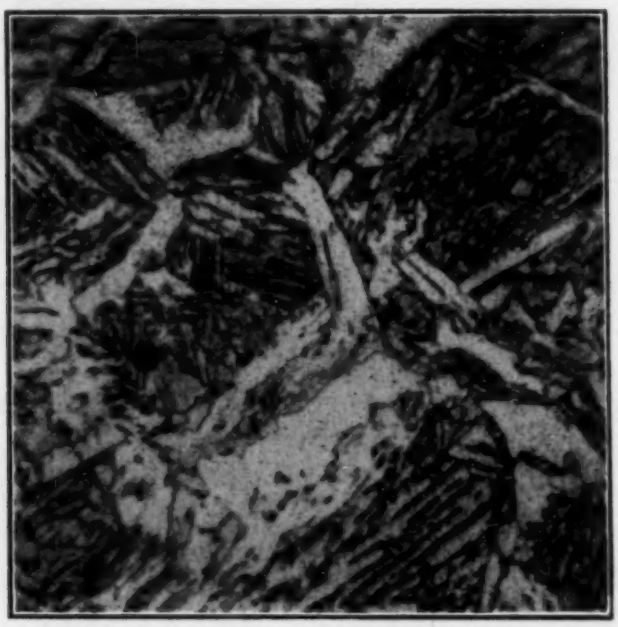


Fig. 6—Typical Structure After Oil Quenching. × 1500. Ferrite—White Areas. Pseudomartensite —Dark Gray Acicular Areas. Martensite—Mottled Gray Areas.

will be seen in Fig. 7 that aluminum increased the ferrite interval. That this implies an increased amount of ferrite is indicated by the increase of ferrite with higher aluminum in the microstructures, shown in Fig. 8. With higher aluminum contents the interval of pseudomartensite formation decreased slightly, and the martensite interval increased. The similarity between the ferrite and martensite curves is apparently due to the enrichment in carbon of the austenite adjacent to the ferrite, in the manner described by Carpenter and Robertson (8). There does not appear to be sufficient time for further migration, and the high carbon enriched austenite is more stable than the austenite of the initial carbon content. The latter, as indicated in Fig. 6, appears to be the core of the original grain and transforms to pseudomartensite, whereas the enriched austenite ad-

jacent to the ferrite areas is more stable and transforms to martensite at a lower temperature. Thus, although aluminum tends to reduce the hardening tendency by causing the rejection of more ferrite and

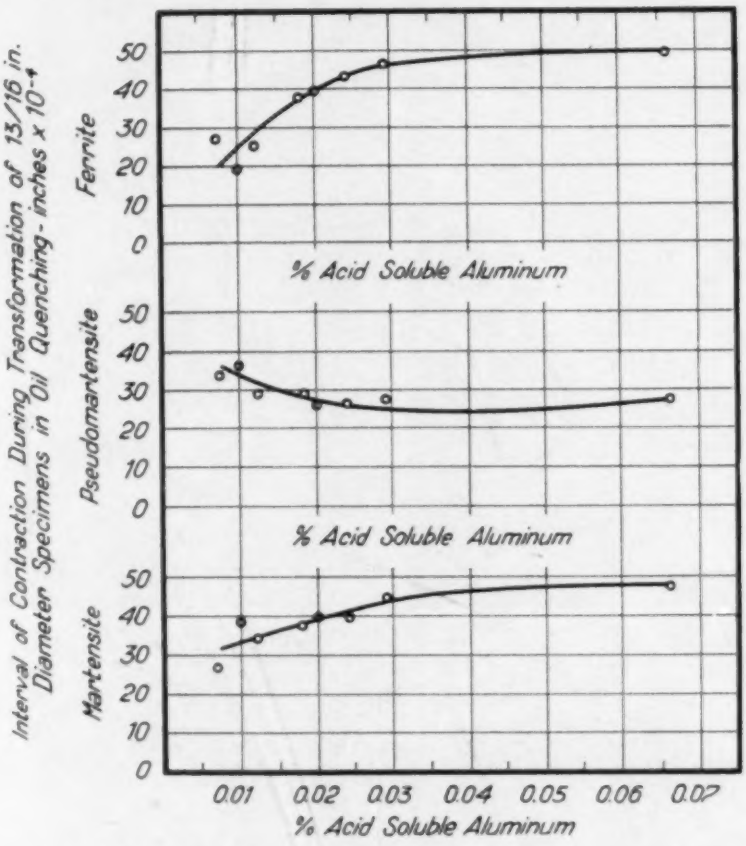


Fig. 7—Effect of Acid Soluble Aluminum Content on Amount of Contraction During Transformation of $\frac{13}{16}$-Inch Diameter Specimens.

the formation of less pseudomartensite, it has a secondary opposing effect of increasing the amount of martensite. This tendency was also confirmed by microscopic examination of the samples.

With vanadium, as shown in Fig. 9, the amount of ferrite and martensite formation reached a maximum at about 0.15 per cent vanadium. The amount of pseudomartensite was quite constant up to about 0.15 per cent vanadium, and increased with higher vanadium contents. Although there was less change in the actual amount of the intervals with vanadium, the ferrite and martensite intervals tended to be lower and the pseudomartensite interval higher than were found in the aluminum series.

In the zirconium-treated steels there was relatively little change, although a slight tendency to higher ferrite and martensite and lower

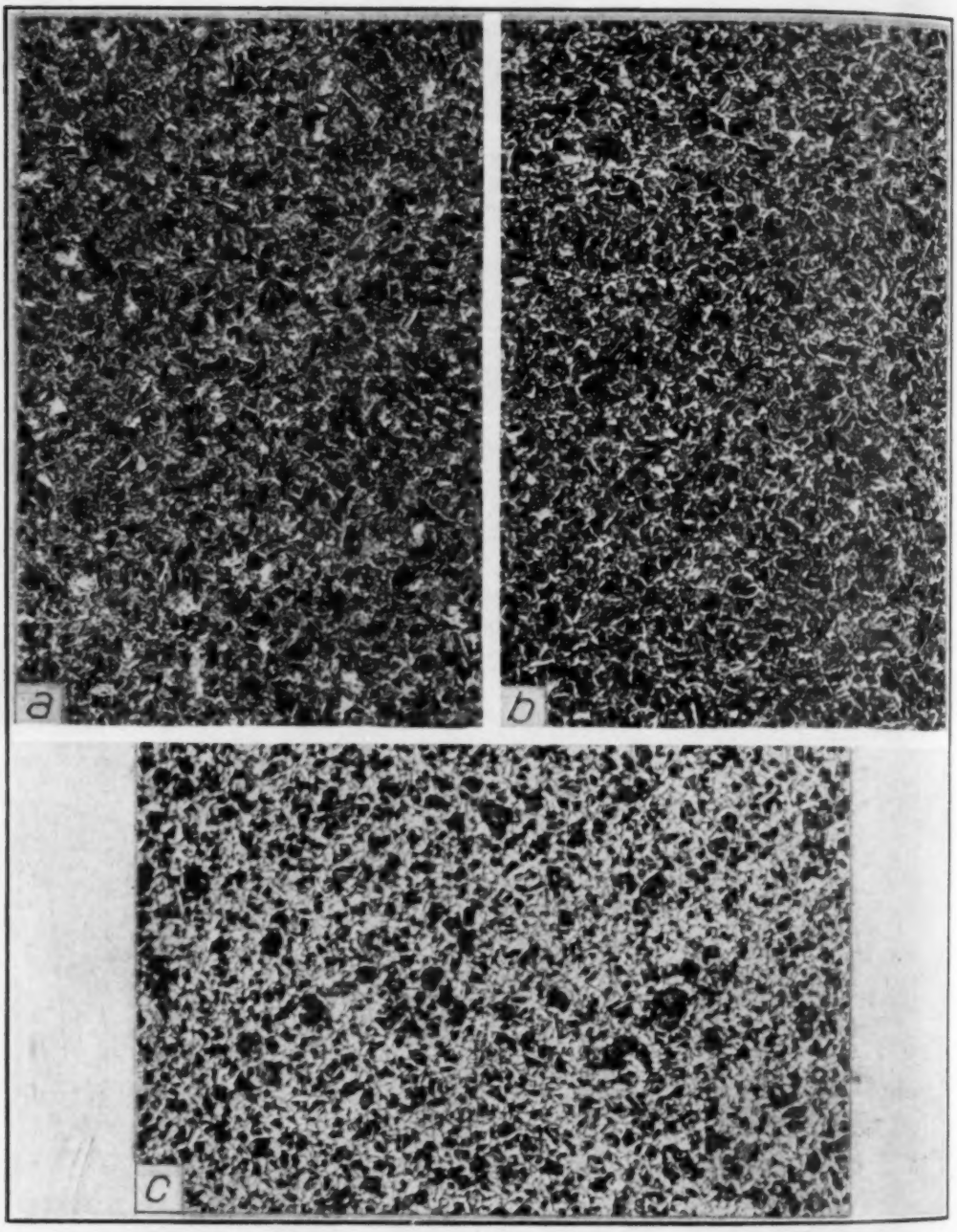


Fig. 8—Microstructure of Oil-Quenched Steels Containing Low, Medium, and High Amounts of Acid Soluble Aluminum. × 100. (a) 0.007 Per Cent Aluminum, (b) 0.018 Per Cent Aluminum, (c) 0.066 Per Cent Aluminum.

pseudomartensite intervals was produced by higher zirconium contents. The actual values were more comparable to those for the vanadium series than to those for the aluminum series. If steels that are not treated with any grain-refining deoxidizer are similar to the very low aluminum steels, it is evident that amounts of

zirconium, smaller than the least amount present in these steels, have a profound effect on the mechanism of transformation.

The correlation of mode of transformation with McQuaid-Ehn grain size is again very poor in the vanadium and zirconium series. There is a tendency toward a general relationship in the aluminum series but it is of a qualitative rather than a quantitative nature.

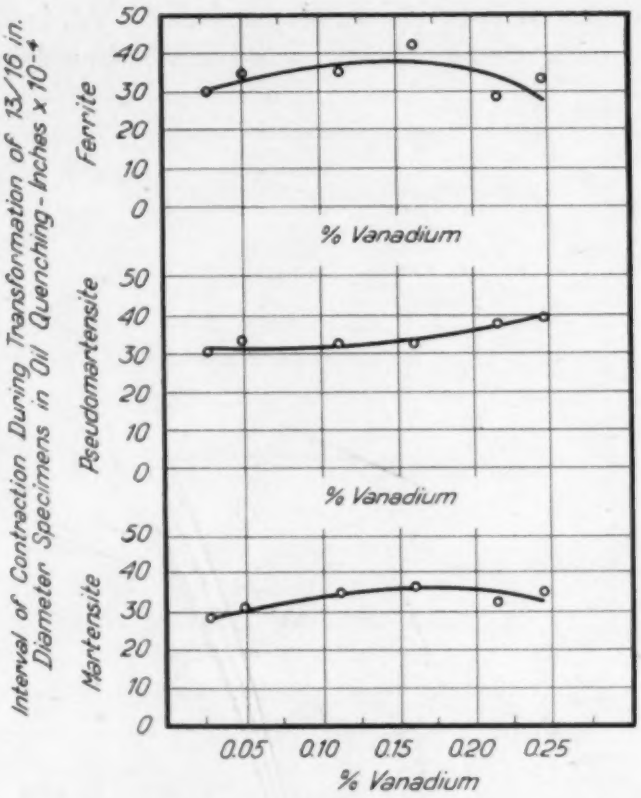


Fig. 9—Effect of Vanadium Content on Amount of Contraction Occurring During Transformation of $\frac{13}{16}$-Inch Diameter Specimens.

Austenite Transformation and Tensile Strength

The relation between actual tensile strength and contraction intervals of ferrite, pseudomartensite and martensite are shown in Fig. 11. As two physical characteristics are being compared, the tensile strength was not corrected for carbon content as was the case in Fig. 3 where tensile strength was compared with deoxidizer content. Although the degree of error is quite large, particularly in the cases of ferrite and martensite, the trends are quite evident. Decrease of ferrite and martensite and increase of pseudomartensite had a well-defined tendency to raise the tensile strength. Further, the

tensile strength was determined by the microstructural components resulting from the austenite transformation and was, therefore, not controlled directly by the grain size or by the amount or kind of deoxidizer.

Austenite Transformation and Distortion

A high degree of correlation, shown in Fig. 12, between distortion and mode of austenite transformation was found in the differ-

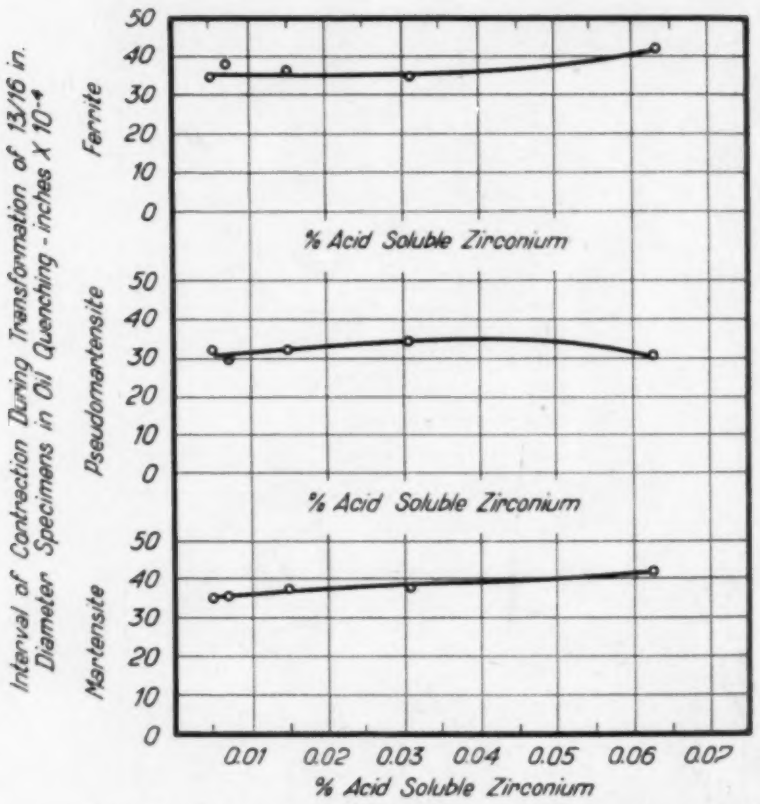


Fig. 10—Effect of Acid Soluble Zirconium on Amount of Contraction Occurring During Transformation of $\frac{13}{16}$-Inch Diameter Specimens.

ences between the transformation intervals of the $\frac{13}{16}$ inch in diameter dilatometric specimen, representing approximately the ¾-inch square section of the base of the tuning fork and the transformation intervals of the ½-inch diameter dilatometric specimen, representing approximately the ¼-inch thick section of the prongs of the tuning fork. In the cases of pseudomartensite and martensite, the amount of distortion was determined by the relative amounts of these constituents formed in the light and heavy sections without respect to

the kind of deoxidizers. In the case of ferrite there was no significant correlation. Trends were present in both aluminum and vanadium steels but were at different levels, and the zirconium steels were quite erratic.

It is evident that the relative amounts of pseudomartensite and

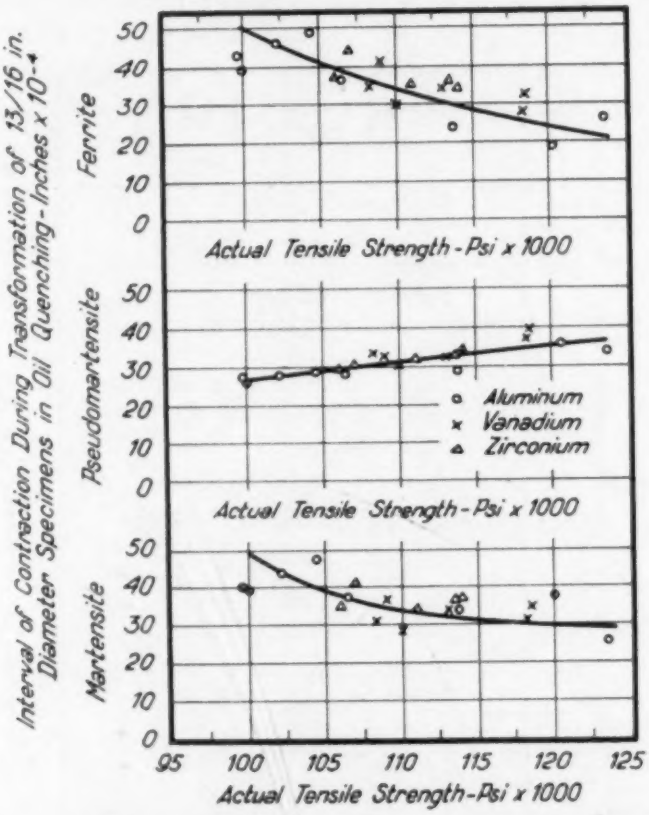


Fig. 11—Relation of Contraction During Transformation of $\frac{13}{16}$-Inch Diameter Specimens to Actual Tensile Strength.

martensite in the light and heavy sections of the tuning fork specimen control the relative movement of the prongs during quenching. More pseudomartensite and less martensite in the heavy base than in the lighter prongs produced a contraction of the distance between the prongs. Similarly, expansion of the prongs resulted from relatively less pseudomartensite and more martensite in the heavy section.

Combined Deoxidizers

As individual deoxidizing elements have such widely varying characteristics, the combinations of properties that may be obtained by treating steel with more than one deoxidizer are of considerable

interest both with respect to properties dependent on the mode of austenite transformation and to the fact that certain combinations of deoxidizers tend to produce sounder steel with greater freedom from large and segregated nonmetallic inclusions. A complete series of 1.5 per cent chromium steels treated with combined deoxidizers is not available so that the properties of 0.15 per cent carbon-1.0 per

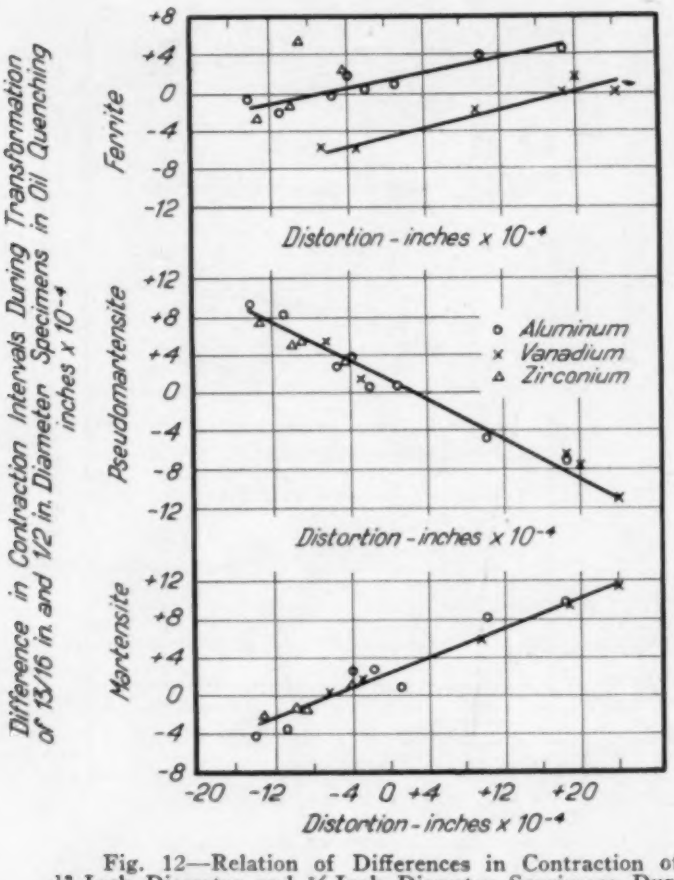


Fig. 12—Relation of Differences in Contraction of 13/16-Inch Diameter and ½-Inch Diameter Specimens During Transformation to Distortion Occurring in Tuning Fork Specimens.

cent chromium steels are described. The steels were treated with ferrosilicon alloys containing appropriate amounts of deoxidizing elements. The deoxidizing additions were made to be equivalent to the amounts of single deoxidizers that produced grain refinement, i.e., 0.06 per cent aluminum, 0.09 per cent zirconium, and 0.12 per cent vanadium. The method of heat treating and testing was the same as in the case of the 1.5 per cent chromium steels.

The results of distortion tests are illustrated in Fig. 13. All of the steels treated with a single deoxidizing element gave positive

distortion. Negative distortion was found in steels treated with complex deoxidizers when the vanadium or zirconium amounts were relatively high and the amount of aluminum was intermediate. Practically no distortion was produced in steels treated with appproximately equal equivalent amounts of deoxidizers.

The tensile strength, illustrated in Fig. 14, also varied with the type of complex deoxidizer. The plain zirconium steels, the plain

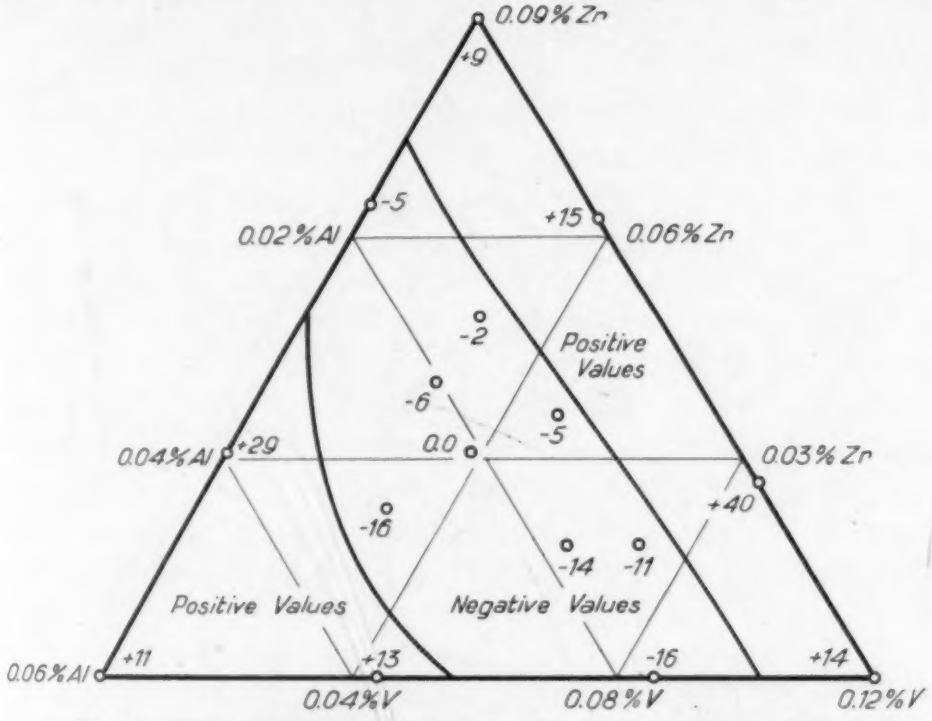


Fig. 13—Effect of Simple and Complex Deoxidizers (added amounts) on Distortion Values of 0.15 Per Cent C—0.50 Per Cent Mn—1.0 Per Cent Cr Steels—Inches × 10^{-4}.

aluminum steels, and those treated with high aluminum-vanadium combinations of deoxidizers gave relatively high strength. Lower tensile strength was produced by plain vanadium and complex deoxidizers containing relatively less vanadium and higher zirconium or aluminum.

Comparison of Figs. 13 and 14 reveal that many combinations of tensile strength and distortion may be obtained by the use of complex deoxidizers. A few such combinations follow:

Distortion	Strength	Al	V	Zr
Negative	Low	Med.	Med.	Med.
Negative	High	Low	High	Low
Positive	Low	—	High	—
Positive	High	High	—	—

Inasmuch as the tensile strength and distortion did not vary in a similar manner, it is apparent that different combinations of deoxidizers do not produce similar changes of austenite transformation in different sections. For this reason it may be concluded that deoxidizers not only change the properties in one section but also have an influence on the effect of mass. The degree to which this property is effective may be inferred from the range of distortion found in the tests of steels treated with both simple and complex deoxidizers.

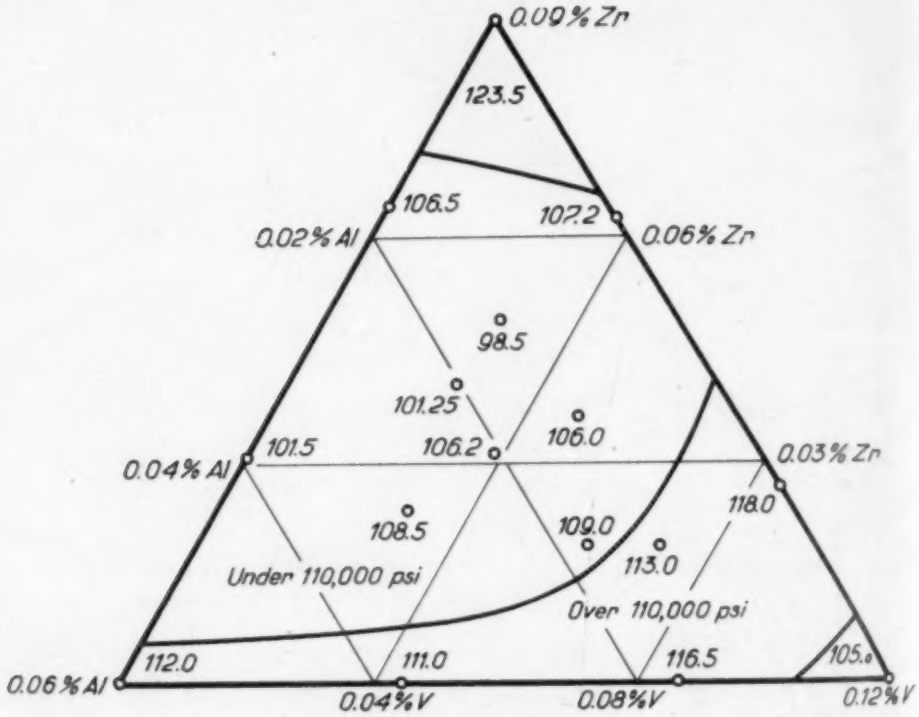


Fig. 14—Effect of Complex Deoxidizing Alloys on Tensile Strength of 0.15 Per Cent C—0.50 Per Cent Mn—1.0 Per Cent Cr Steels—Pounds Per Square Inch × 1000.

Summary

In summarizing this study of the grain-refining deoxidizers, aluminum, vanadium, and zirconium, in low carbon, 1.5 per cent chromium steel it is evident that:

1. McQuaid-Ehn grain size is not directly related to the amount of acid-soluble residual deoxidizer. A tendency to some correlation between grain size and the properties of the aluminum-treated steels was observed, but even this degree of relationship was not found in the vanadium and zirconium series.

2. The products of the austenite transformation during quench-

ing vary with the amount and kind of residual acid-soluble deoxidizing element. Aluminum tends to increase the amount of ferrite and martensite, and to decrease the amount of pseudomartensite. Vanadium tends to produce a maximum of ferrite and martensite at about 0.15 per cent vanadium, and to increase the amount of pseudomartensite at high vanadium contents. Increase of zirconium produces relatively small changes. The effects of very small amounts of zirconium, however, must be quite large to produce the pronounced difference between the lowest zirconium steel and the corresponding very low aluminum steels.

3. The tensile strength is determined by the amount of ferrite, pseudomartensite, and martensite, and only indirectly by the amount and kind of deoxidizing element. The strength was increased by less ferrite and martensite, and more pseudomartensite. Through their effects on the mechanism of transformation aluminum decreased, vanadium increased, and zirconium lowered the tensile strength.

4. The distortion during quenching of the tuning fork specimen is determined by the difference in the amounts of pseudomartensite and martensite formed in the heavy base as compared with the lighter prong. Relatively less pseudomartensite and more martensite in the heavy base caused an increase in the distance between the prongs. Continuous changes of distortion characteristics were produced by the grain-refining elements in proportion to their effects on the austenite transformation.

It would appear that the properties tested, and presumably others as well, are primarily dependent on the mechanism of austenite transformation. In turn the transformation of austenite, other things being constant, is determined by the amount and kind of deoxidizer that is present in the steel in an acid-soluble form probably as an alloy, a metallic compound, or a nonmetallic compound in a very fine state of subdivision. For this reason, accurate control of the residual amounts of single deoxidizers, and the use of complex deoxidizers offer a means of more consistently obtaining desirable combinations of properties. Obviously the quantitative results of this investigation are limited to the specific conditions under which the work was carried out. Different compositions, manufacturing and heat treating conditions, sizes and proportions of specimens, and many other factors would change the results quantitatively but there is no reason to believe that comparable differences would not be produced under other conditions.

Acknowledgments

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DEVELOPMENT IN MOLYBDENUM HIGH SPEED CUTTING STEELS

By Walter R. Breeler

Abstract

Within the past ten years the use of molybdenum high speed steel has been steadily increasing. The most popular analysis at the present time is: Carbon 0.72 to 0.81, silicon 0.20 to 0.45, manganese 0.30 maximum, chromium 3.50 to 4.00, tungsten 1.30 to 1.80, vanadium 0.90 to 1.30, molybdenum 8.00 to 9.50. When this steel was first introduced several objections were raised, the main one being the tendency to decarburize more than 18-4-1. Numerous modified compositions were developed in an attempt to overcome these objections. The more important of these new steels are listed in the article and discussed from the standpoint of manufacturing, decarburization, and cutting ability. The attempts to produce a better steel involved the use of copper and boron or both, omitting tungsten and substituting vanadium, and changing the ratio and amounts of tungsten and molybdenum.

FOR the past ten years, in the tool and tool steel industries the interest shown in molybdenum high speed steels has been steadily increasing. The subject is actually an old one, since the possibilities of using molybdenum in cutting steels have been known for more than thirty years. A good description of the history and development of these materials up to 1932 is contained in J. L. Gregg's book entitled, "Alloys of Iron and Molybdenum." Many individuals and organizations have contributed to this development, but special recognition should be accorded the work at Watertown Arsenal, the introduction of Mo-Tung by the Universal Steel Company, J. V. Emmons' contributions to the literature and the advent of Mo-Max.

It is not the purpose of this paper to compare molybdenum high speed steels with 18-4-1, but rather to appraise the various modifications that have come into existence since the introduction of the molybdenum-tungsten type of the following general analysis: Car-

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bon 0.72 to 0.81, silicon 0.20 to 0.45, manganese 0.30 maximum, chromium 3.50 to 4.00, tungsten 1.30 to 1.80, vanadium 0.90 to 1.30, and molybdenum 8.00 to 9.50.

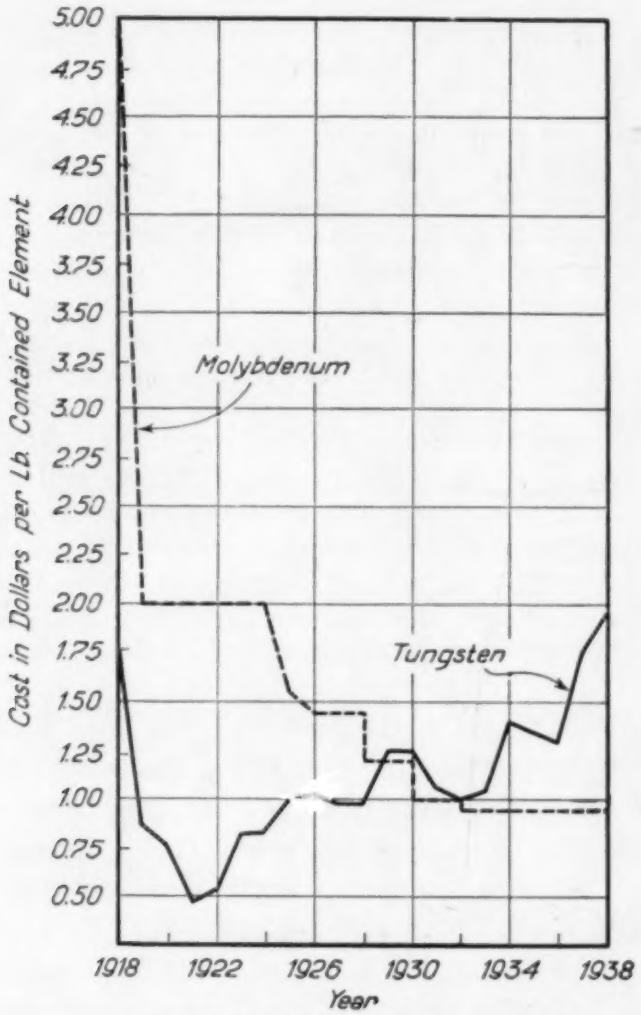


Fig. 1—Average Yearly Prices of Ferrotungsten and Ferromolybdenum. 1918-1938.

The favorable showing made to date indicates that molybdenum high speed steels are here to stay. Just how far they will replace 18-4-1 depends upon circumstances beyond our immediate control or prediction. However, we do know that the amount used has been steadily increasing these past five years. This type of tool steel represents an economically stable and secure product. Molybdenum is available in this country in ample quantities, and the price has not fluctuated like that of tungsten. Fig. 1 shows the relative prices of the two elements over a 20-year period.

Following the experience of most new products, molybdenum-tungsten high speed steel had certain objections to overcome. However, by co-operative effort on the part of steel manufacturer, consumer, and equipment maker, most of the early troubles have been corrected. Manufacturing difficulties have been minimized and today a high quality product is being produced. Decarburization limits on hot-rolled bars are the same as for 18-4-1, but in order to maintain these limits, ingots and billets must be covered with borax or some other coating at all heating operations. The cutting ability of molybdenum-tungsten high speed steel has improved steadily with the improvement in quality and heat treating technique, and in many cases it is performing better than high tungsten steel. This applies chiefly to the products of tool manufacturers who have special heating equipment and metallurgical control. The average industrial consumer is not so well equipped, and in this field molybdenum high speed steels will require more time to become established.

As soon as it was realized that the molybdenum-tungsten steel was becoming an important factor in the tool steel industry, other types were developed. The three main reasons prompting these developments were as follows, and will be discussed in greater detail:

(1) To overcome, or at least decidedly reduce, the tendency to decarburize.

(2) To produce a better cutting steel with molybdenum as the predominating alloying element.

(3) To produce an acceptable molybdenum cutting steel outside of existing patents.

(1) One of the first criticisms heard about molybdenum high speed steels was their tendency to decarburize when heat treated in an open or semi-muffle furnace without special attention to atmosphere or provision of some coating on the work. It must be admitted that the problem of decarburization is becoming much less serious than it was several years ago, but it still cannot be entirely ignored. The various successful heat treating methods now in use are as follows:

(a) Protecting tools with borax usually produces good results. The disadvantages are (1) time required to prepare borax, apply and remove, and (2) attack of furnace refractories.

(b) Salt baths are quite successful. Some installations are still not entirely satisfactory, and produce pitting, solution of steel, and decarburization. Apparently all of these troubles

can be overcome by adhering to instructions issued by the salt manufacturers and furnace builders.

(c) Graphite composition muffles are used advantageously for small tools, although there is a slight tendency to carburize.

(d) Special atmospheres in muffle furnaces, produced by burning gas and air and containing from 6 to 11 per cent CO, are quite satisfactory for small tools. For example, ½-inch square tool bits can be heat treated with less than 0.002 inch soft surface. This equipment, however, is still not good enough for large tools or small ones with fine edges. Some consideration is being given to atmospheres generated outside of the furnace and containing high percentages of CO, nitrogen, or both. A suitable atmosphere, generated in a reasonably priced unit, could be used advantageously in connection with muffle furnaces, and eliminate the use of borax.

(e) Another very recent experiment consists of introducing into the heating chamber a chemical compound forming a vapor, which in turn condenses on the tools being treated, thereby preventing decarburization.

(2) In an effort to produce a better cutting steel with molybdenum as the main alloying element, changes were made in the original molybdenum-tungsten steel analysis, involving small additions or omissions. Except for the addition of cobalt, these changes have not yet proven to be effective or practical.

(3) The third motive was to provide an acceptable molybdenum steel outside of existing patents. Such a course does not change the general patent situation, since any new steel developed is usually patented. But the fact that these situations stimulate research will probably result in some ultimate good to the industry.

Materials that have been developed these past six years, and which represent a modification or an attempt to produce a better molybdenum steel to sell at approximately the same price as the molybdenum-tungsten type, fall within the following general classifications:

(1) Molybdenum-2 per cent vanadium high speed steel.

(2) Molybdenum-vanadium and molybdenum-tungsten steel, with boron.

(3) Molybdenum-vanadium and molybdenum-tungsten steel, with boron and copper.

(4) Steel containing approximately 6 per cent tungsten, 6 per cent molybdenum, 4 per cent chromium, 1.5 per cent vanadium, and 2.5 per cent copper.

(5) Steel containing 4 to 6 per cent tungsten, 3.5 to 6 per cent molybdenum, 4 per cent chromium, and 1 to 1.6 per cent vanadium.

Steels 2, 3, 4, and 5 had for their chief aim the reduction of decarburization, plus any cutting advantage possible.

Although the molybdenum-tungsten-cobalt compositions represent an improved molybdenum cutting steel, they have been omitted from the above list for several reasons: (1) They are of sufficient importance as an improved molybdenum steel to constitute a subject by themselves, and (2) the addition of 4 to 10 per cent cobalt places them outside of the price class of materials to be discussed in this article.

Some of the materials in the list were short-lived and are now obsolete, but are of interest since they represent definite steps in attempting to improve the molybdenum-tungsten type.

In the paragraphs to follow, the various steels will be discussed chiefly from the standpoint of manufacturing, decarburization, and cutting ability. The information on performance represents a cross section of data obtained from laboratory tests, reports from tool manufacturers and some industrial users of molybdenum steels. In some instances, due to insufficient data, the conclusions can only serve to indicate a trend or prediction which may or may not be reversed as additional performance reports are received.

Steel No. 1

Molybdenum-2.00 Per Cent Vanadium High Speed Steels

The use of molybdenum-vanadium cutting steels anticipated the present molybdenum-tungsten type by quite a few years. One analysis in particular received considerable attention at Watertown Arsenal. This work indicated that at the time the best all-purpose composition was as follows: Carbon 0.68, manganese 0.25, silicon 0.25, chromium 3.50, molybdenum 9.50, vanadium 1.25. For heavy planer tools and very heavy lathe tools the molybdenum steel was found to be about 90 per cent as efficient as the standard tungsten high speed steel. For smaller planer, lathe, and form cutters the

molybdenum steel was found to be practically as efficient as the tungsten type. U.S. patent 1,345,732, issued July 6, 1920, to Arnold, discloses an alloy of the following composition limits: Carbon 0.50 to 0.80, manganese 0.10 to 0.30, silicon 0.20 to 0.50, chromium 2.75 to 3.75, vanadium 0.50 to 2.00, molybdenum 5.00 to 10.00. U.S. patent 1,448,288, issued March 13, 1923, to Eilender, covers the following: Carbon 0.50 to 0.80, molybdenum 6.00 to 10.00, chromium 3.00 to 6.00, manganese 0.20 to 0.40, silicon 0.20 to 0.40, vanadium 0.15 to 2.00. In 1916, the following analysis was reported developed in Germany: Carbon 0.50 to 0.80, molybdenum 6.00 to 10.00, chromium 3.00 to 6.00, vanadium 0.75 to 2.00, cobalt 1.50 to 3.50. Patents have more recently been issued to Kingsbury and Gill covering molybdenum-vanadium compositions.

Types 1 and 2, shown below, represent the popular analysis ranges used the past six years:

	Type 1	Type 2
Carbon	0.75-0.90	0.75-0.90
Manganese	0.20-0.40	0.20-0.40
Silicon	0.20-0.40	0.20-0.40
Chromium	3.50-4.50	3.50-4.50
Vanadium	1.70-2.00	2.00-2.30
Molybdenum	7.00-8.50	8.50-9.50

The manufacturing practice for the molybdenum-vanadium steels is about the same as for the molybdenum-tungsten type, and a good quality product can be made.

Cutting Tests—It is claimed by some users that the higher molybdenum and vanadium in Type 2 analysis contribute better cutting properties. Drills, giving exceptionally good performance in a laboratory test, were made from the following steel: Carbon 0.89, vanadium 2.20, chromium 3.85, molybdenum 9.68. However, considerable of Type 1 analysis has also been found satisfactory for certain tools. In an accelerated lathe breakdown test in which a ⅜-inch square tool travels from the center of a disk to the periphery, Type 2 molybdenum-vanadium steel failed at 312 surface feet per minute and the molybdenum-tungsten tool failed at 311. In another lathe test, ⅝-inch square tools were used for turning S.A.E. 2335 steel, 194 Brinell, with soluble oil coolant. Tool angles were ground by machine and the depth of cut was ⅛ inch, feed 0.037 inch, and speed 120 surface feet per minute. Under these conditions the tools cut as follows before failure:

Type Analysis	Time—average of 3 tools
1. 8.50 molybdenum, 1.00 vanadium, 1.50 tungsten	7 minutes 45 seconds
2. 9.00 molybdenum, 2.00 vanadium	7 minutes 42 seconds

Although some laboratory tests indicate performance comparable to molybdenum-tungsten steel tools, commercial reports on drills, cutters, taps and tool bits are too few and conflicting to make possible a general statement of this kind.

Impact Tests—When the molybdenum-vanadium materials were first tried, there was some question of adequate toughness. It was also reported that increasing the molybdenum from 7.00 or 8.00 to 9.00 or 10 per cent would embrittle the steel. All cutting tools in laboratory tests and those returned from customers were watched to

Table I
Izod Impact Tests
Specimens Unnotched

Values are average of four determinations

Steel	Analysis Table Per Cent C	Mn	Si	Cr	V	Mo	W
1	0.83	0.42	0.26	3.72	2.18	8.80	....
2	0.82	0.31	0.32	3.78	2.20	9.73	....
3	0.78	0.26	0.23	3.81	1.07	8.97	1.77

Heat treatment of specimens: Preheat 1600 degrees Fahr.—15 minutes, high heat 2200 degrees Fahr.—2 minutes, oil quench.
Tempering time 2 hours—electric circulating air furnace.

Degrees Fahr. Draw	Steel 1 Rockwell C Hardness	Steel 1 Ft.-Lbs. Absorbed Impact Value	Steel 2 Rockwell C Hardness	Steel 2 Ft.-Lbs. Absorbed Impact Value	Steel 3 Rockwell C Hardness	Steel 3 Ft.-Lbs. Absorbed Impact Value
0	64.5	18.3	65.0	32.3	66.3	11.5
500	61.0	30.3	61.5	31.5	62.0	20.8
700	61.0	24.0	62.0	33.5	62.6	26.3
900	63.0	20.8	63.0	26.5	63.6	20.3
950	65.0	18.0	64.5	20.5	65.6	16.0
1000	64.5	16.3	64.5	13.5	65.6	13.3
1050	64.0	12.5	63.5	19.8	64.6	12.8
1100	61.0	12.3	60.0	16.5	62.8	15.2
1200	56.0	16.5	56.0	23.5	58.0	25.5

see if there was any sign of brittleness, and to date no such indications have been reported. We therefore assume that for all practical purposes there is little difference in toughness between the two types of molybdenum-vanadium and molybdenum-tungsten steels. However, in order to find out more about this property, Izod impact tests were made and the results are shown in Table I. In the range of maximum secondary hardness there is little difference between any of the steels. Another comparison was made at a hardening temperature of 2250 degrees Fahr. and the same relationship existed, although all values were lower.

Decarburization—One of the earliest observations noted in comparing molybdenum-vanadium with molybdenum-tungsten steel was

the greater amount of decarburization when heat treated in a muffle or semi-muffle furnace. The absence of tungsten and the presence of higher vanadium aggravated the decarburizing effect of high molybdenum. In Table II will be found a number of tests in which samples of both steels were run together under various furnace conditions. These results are typical of a number of reports received from tool manufacturers. If borax coating or salt baths are used under proper conditions, there is no appreciable decarburization with either steel.

Table II
Decarburization Test
Molybdenum-Vanadium vs. Molybdenum-Tungsten
Steels 1 and 3 from Table I

Specimens ⅜ Inch Square x 3 Inches Long

Each test run separately. Table shows conditions of test and amount of total microscopic decarburization. A clean, machined and ground surface was used to start with.

Test	Preheat Minutes	High Heat Degrees Fahr.	Time Minutes	Furnace	Decarb. in 0.001 In. Mo-V	Mo-W
1	1600 Degrees Fahr.—15	2100	4	Muffle-atmosphere 6% CO	0.001	0.001
		2200	4	"	0.003	0.001
		2300	4	"	0.003	0.001
2	1500 Degrees Fahr.—15	2200	10	Semi-muffle 1% O_2	0.016	0.012
3	1500 Degrees Fahr.—15	2250	5	"	0.010	0.006
4	1500 Degrees Fahr.—15	2200	10	"	0.014	0.012

Excepting for a greater tendency to decarburize, the molybdenum-vanadium steels are quite similar in physical properties to the molybdenum-tungsten type. Performance data on drills, cutters, taps and lathe tools are too few and conflicting to attempt any comparison at this time.

Steel No. 2

Molybdenum-Tungsten and Molybdenum-Vanadium Steels with Boron

Several rather comprehensive investigations were started about five years ago to determine the effect of boron in molybdenum high speed steels. Boron is an unusual element in its effect, and small additions were found to be potent. Table III covers a partial list of the compositions studied. There will not be any distinction made between the molybdenum-tungsten and molybdenum-vanadium types since the effect of boron appears to be the same in both.

Within the range studied, boron supplemented carbon in producing hardness as quenched and was approximately one-half as effective.

For example, the usual molybdenum-tungsten steel with 0.80 per cent carbon and no boron hardened to 66-67 C Rockwell. This hardness could also be obtained with 0.60 per cent carbon and 0.40 per cent boron, or 0.50 per cent carbon and 0.60 per cent boron. If one-half

Table III
Molybdenum-Tungsten and Molybdenum-Vanadium Steels with Boron

Steel No.	Analysis									Per Cent Recovery in 4 Inch Square Billets
	C	Mn	Si	W	Cr	V	Mo	Co	B	
1	0.85	0.52	0.54	1.75	5.05	1.82	10.52	....	0.041	34.8
2	0.72	0.28	0.29	1.51	3.38	2.14	8.23	....	0.05	51.0
3	0.79	0.45	0.42	1.66	4.17	1.74	9.80	....	0.06	none
4	0.78	0.42	0.31	2.12	4.05	1.79	9.88	....	0.08	69.8
5	0.805	0.55	0.53	1.75	4.34	1.66	9.62	....	0.08	15.3
6	0.82	0.49	0.44	1.85	4.64	1.80	10.60	....	0.09	25.3
7	0.75	0.52	0.92	1.98	4.44	1.66	9.40	....	0.09	50.0
8	0.75	0.42	0.34	1.71	3.98	1.50	8.64	....	0.10	none
9	0.48	0.54	0.78	1.31	4.54	1.22	9.54	....	0.15	none
10	0.82	0.41	0.50	1.73	4.53	1.65	9.36	....	0.16	none
11	0.61	0.34	0.60	1.65	4.64	1.17	8.72	....	0.19	74.0
12	0.48	0.29	0.50	1.71	4.56	1.20	10.13	....	0.20	50.0
13	0.78	0.35	0.48	1.59	3.72	2.20	8.47	....	0.23	none
14	0.56	0.34	0.68	1.69	3.92	1.23	9.76	....	0.24	31.0
15	0.47	0.27	0.61	1.50	4.17	1.14	9.04	....	0.27	18.0
16	0.52	0.50	0.82	1.27	4.07	1.08	8.66	....	0.28	none
17	0.53	0.62	0.80	1.19	4.58	1.34	9.40	....	0.31	none
18	0.67	0.52	0.41	1.43	4.23	1.60	9.95	....	0.32	11.7
19	0.64	0.50	0.81	nil	4.51	1.39	7.92	....	0.66	none
20	0.63	0.42	1.01	nil	4.51	1.57	9.36	....	0.77	none
21	0.80	0.19	0.29	1.52	3.81	1.08	8.67	....	nil	....
22	0.84	0.26	0.68	1.39	3.61	1.50	9.62	....	nil	....
23	0.81	0.32	0.23	1.48	4.08	1.28	8.45	....	nil	....
24	0.77	0.28	0.78	2.04	3.92	2.41	9.09	....	0.15	....
25	0.80	0.30	0.75	1.66	4.00	2.62	8.45	....	0.19	....
26	0.58	0.37	0.62	1.60	4.21	1.34	8.83	....	0.19	....
27	0.83	0.27	0.30	1.85	4.11	2.34	8.63	....	0.21	....
28	0.48	0.23	0.46	1.57	4.11	1.20	8.78	....	0.29	....
29	0.76	0.23	0.85	1.70	4.09	2.27	8.13	....	0.39	....
30	0.63	0.32	0.52	1.47	4.06	1.36	8.47	....	0.40	....
31	0.43	0.23	0.49	nil	4.06	1.18	8.77	....	0.41	....
32	0.45	0.27	0.49	4.57	4.52	2.15	5.51	....	0.42	....
33	0.40	0.22	0.52	1.50	4.04	1.19	8.73	....	0.46	....
34	0.49	0.25	0.63	1.53	4.17	2.20	8.84	....	0.46	....
35	0.54	0.78	0.60	1.60	4.14	1.19	8.63	....	0.46	....
36	0.54	1.65	0.78	1.56	4.18	1.20	8.77	....	0.46	....
37	0.51	0.22	0.50	nil	4.09	2.27	7.50	....	0.48	....
38	0.81	0.25	0.62	1.86	4.00	2.03	9.33	....	0.49	....
39	0.83	0.28	0.52	1.57	4.15	1.28	8.87	....	0.53	....
40	0.48	0.26	0.55	1.67	4.12	1.17	8.74	....	0.64	....
41	0.58	0.17	0.38	nil	3.85	2.10	9.17	4.28	0.33	....
42	0.43	0.25	0.45	1.73	4.01	1.22	9.08	5.10	0.42	....
43	0.45	0.25	0.60	nil	4.14	1.17	8.58	5.10	0.46	....
44	0.64	0.24	0.61	1.80	3.98	2.24	9.07	6.75	0.49	....

of the boron content added to the carbon content equaled approximately 0.80, maximum hardness was obtained. However, boron added to a 0.80 per cent carbon steel did not increase hardness beyond 66-67. When replacing substantial amounts of carbon in the above proportions, boron was not only effective in producing high initial hardness as quenched but aided in maintaining high secondary hardness up to 1000 degrees Fahr. Beyond this point the boron steels

decreased in hardness slightly more rapidly than material of equivalent carbon content. Practically all the boron steels showed a coarse fracture when hardened at 2200 degrees Fahr. and above and with a carbon content of about 0.80 per cent the microstructure indicated formation of eutectic as low as 2100 degrees Fahr. Fig. 2 shows a

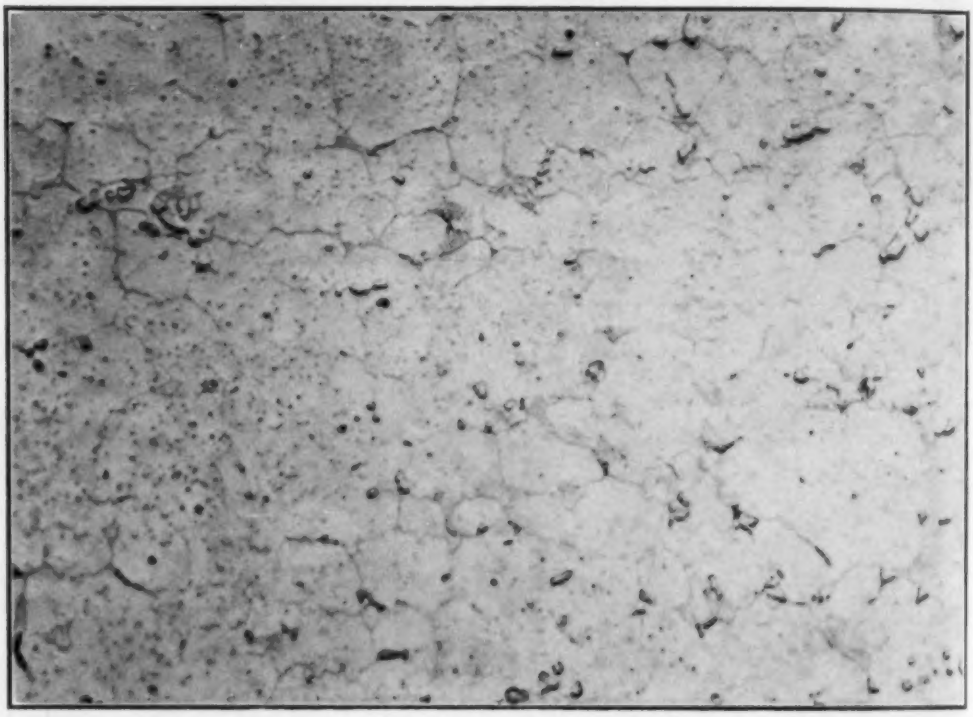


Fig. 2—Steel No. 25—Oil Quench 2150 Degrees Fahr.—Eutectic at Grain Boundaries. × 500.
Analysis:

C	W	Cr	V	Mo	B
0.80	1.66	4.00	2.62	8.45	0.19

typical structure of a boron steel hardened at 2150 degrees Fahr. The best hardening range was therefore under 2200 degrees Fahr., and was obviously very narrow. The addition of vanadium appeared to slightly elevate the permissible hardening range.

Manufacture—In the early part of the investigation, considerable experimenting had to be done to determine the right forging range and method of forging. Several of the very low recovery figures in Table III would have been higher if there had been a better background of experience. The best forging temperature was found to be between 1900 and 2000 degrees Fahr. At this temperature the metal was fairly stiff and many reheatings are necessary when cogging an 8-inch ingot to a 4-inch square billet. With carbon at 0.70 to 0.80 and boron 0.05 per cent or more, forging was difficult and the recov-

eries were erratic and usually very low. With carbon under 0.60 per cent and boron under 0.50 per cent, forging of small ingots was reasonably satisfactory and encouraging. With large ingots even this carbon and boron content did not produce very satisfactory results. Some improvement in forging was noticed if the ingots were transferred to the forging furnace shortly after casting. However, this practice is not always practical and all of the recovery figures given in Table III are for 8-inch and 9-inch ingots that were cooled to room temperature after casting, then annealed at 1500 degrees Fahr. before placing in the forging furnace. All ingots were preheated carefully before raising to the high temperature.

Table IV
Effect of Boron on Decarburization as Determined by Microscope

Steel No.	Boron Content	Test 1 2200°—2' Semi-Muffle Furnace 1% O_2	Test 2 2200°—2' Semi-Muffle Furnace 1% O_2	Test 3 2200°—3' Muffle Oxidizing	Test 4 2250°—2' Muffle 6% CO	Test 5 2250°—5' Muffle 6% CO	Test 6 2150°—4' Semi-Muffle 1% O_2
21	nil	.....	0.005	.....	0.001	0.006	0.005 to 0.006
2	0.05	0.004	0.004	0.0025	.....	.....	.....
4	0.08	.....	.....	.....	0.001	0.004	.....
24	0.15	.....	0.000 to 0.002	.....	.....	.....	.....
25	0.19	trace	.....	trace—0.003	.....	.....	0.003 to 0.005
27	0.21	.....	0.000 to 0.003	.....	.....	.....	.....
29	0.39	trace	.....	trace—0.0025	.....	.....	.....
38	0.49	trace	.....	trace	.....	.....	.....
39	0.53	.....	.....	trace	.....	.....	.....

Considerable time and effort were spent in trying to overcome forging difficulties, and about the only improvement noted was with the addition of cobalt. High silicon appeared to be detrimental, and best results were obtained when this element was under 0.30 per cent. When forging many of the boron ingots, the center appeared to granulate and a steady flow of red-hot particles kept coming out of the pipe end. This necessitated cutting back, and quite often the whole ingot would be ruined in this manner.

Decarburization—It was noted early in the investigation that boron would have some beneficial effect on decarburization. Up to about 0.10 per cent there is only very slight improvement. At 0.20 per cent boron the improvement is noticeable, but still not entirely satisfactory. At 0.40 to 0.50 per cent boron there is a marked improvement, and for most ordinary hardening conditions the steel would be considered practically free from decarburization. With all

the alloys containing boron the decarburization has a tendency to be spotty. Table IV shows some typical results. The table is separated into various tests carried out by different investigators and in different furnaces.

Cutting Tests—Due to manufacturing difficulties, only a limited amount of material was available for laboratory and commercial tests. Typical laboratory results are shown in Tables V and VI. Although

Table V

Tool Bits ⅞x¾x5½ Inches
Cut Started at Center of 11-Inch Diameter Disk and Tool Bit Moved Toward Periphery

Analysis									Speed at Failure Feet Per Minute	
C	Mn	Si	W	Cr	V	Mo	Co	B	Test 1	Test 2
0.81	0.32	0.23	1.48	4.08	1.28	8.45	....	nil	211	161
0.71	0.30	0.27	1.51	3.64	2.02	8.14	....	0.05	...	164
0.80	0.30	0.75	1.66	4.00	2.62	8.45	....	0.19	...	172
0.58	0.17	0.38	nil	3.85	2.10	9.17	4.28	0.33	228	...
0.63	0.32	0.52	1.47	4.06	1.36	8.47	....	0.40	206	...
0.81	0.25	0.62	1.86	4.00	2.03	9.33	....	0.49	196	...
0.64	0.24	0.61	1.80	3.98	2.24	9.07	6.75	0.49	213	...

Table VI

⅝-Inch Square Tool Bits
Test Log S.A.E. 2335—Brinell 213/220—Soluble Oil Coolant
Speed—120 Ft. per Min.; Depth of Cut—⅛ Inch; Feed—0.037 Inch

(Average of 2 Grinds)

Analysis								Average Length of Cutting Time Before Failure
C	Mn	Si	W	Cr	V	Mo	B	
0.84	0.26	0.68	1.39	3.61	1.50	9.62	nil	16′—12″
0.78	0.42	0.31	2.12	4.05	1.79	9.28	0.08	21′—15″

data on this property are limited, it is the consensus of opinion of several investigators that boron up to 0.50 per cent provided only a slight advantage in cutting ability when added to a molybdenum-tungsten or molybdenum-vanadium steel. This opinion is further indicated in the discussion of copper-boron steels. Adding cobalt with boron appeared to be a very good combination, and a steel that has shown exceptional merit for the past several years analyzes carbon 0.60 per cent, tungsten 1.73 per cent, chromium 4.86 per cent, vanadium 1.61 per cent, molybdenum 8.62 per cent, cobalt 8.23 per cent, and boron 0.27 per cent.

Impacts—A few series of impact tests were made, and it was noted that the addition of boron to molybdenum-tungsten or molybdenum-vanadium steels did not materially affect this property. In fact, with an alloy containing 0.40 per cent carbon and 0.60 per cent boron the impacts were slightly better than the equivalent 0.70 per cent carbon steel.

Indications to date are that boron additions to molybdenum-

tungsten or molybdenum-vanadium high speed steel do not improve the alloy sufficiently to warrant the extra expense. However, more information on alloys in the range of 0.60 per cent carbon and 0.40 per cent boron would be of interest. With the boron steels studied in this report, the advantages were:

(1) Decreased decarburization.
(2) Perhaps slightly better performance.

Outstanding disadvantages were:

(1) Poor forgeability.
(2) Cost of boron.
(3) Loss of boron in melting.
(4) Erratic recovery of boron in melting.
(5) Difficulty in analyzing for boron.
(6) Narrow hardening range.

Steel No. 3

Molybdenum-Tungsten and Molybdenum-Vanadium Steels with Copper and Boron

From carburizing experience, it was known that a copper coating would prevent or retard penetration of carbon. It was thought that if copper were alloyed with a steel having a marked tendency to decarburize, loss of carbon would be prevented. With a steel containing 8.00 to 9.00 per cent molybdenum, it was found that copper alone, in reasonable quantities (up to 3.00 per cent), would not accomplish this purpose to the desired degree. It was therefore decided to combine copper with boron and have the two elements supplement or combine their effects. After much experimenting, the optimum amounts of each were determined and a steel was produced that was practically free from decarburization when heat treated by any ordinary method. A typical analysis, representing the best combination of alloys, was as follows:

	Per Cent
Carbon	0.73-0.83
Manganese	0.35-0.65
Silicon	0.10-0.25
Chromium	3.50-4.25
Molybdenum	7.75-9.00
Tungsten	1.50-2.25
Vanadium	0.90-1.30
Copper	2.60-3.00
Boron	0.07-0.12

Manufacture—About twelve heats of 8-inch ingots were made and the forging recovery figures are shown in Table VII. Copper

did not prove to be an aid in overcoming the forging trouble caused by boron, and about the same difficulties were encountered. The forging procedure and temperature were the same as described under boron steels. The recoveries were erratic and very low in many cases. One or two steels produced good yields, but the billets had to be

Table VII
Recovery Percentages of Copper-Boron Steels
8-Inch Ingot to 4-Inch Square Billet

Type Analysis:

	C	Mn	Si	Cr	V	W	Mo	Cu	B
Group 1	0.80	0.50	0.30	4.00	1.00	1.75	8.50	2.80	See below
Group 2	0.80	0.50	0.30	4.00	1.75	....	9.25	2.75	See below

Boron Content	Group 1 Recovery in 4 Inch Square Per Cent	Group 2 Recovery in 4 Inch Square Per Cent
0.02	67	..
0.03	75	..
0.04	..	18
0.05	80	..
0.07	..	24
0.08	..	49
0.12	0	..
0.14	..	48
0.15	..	60
0.17	0	..
0.18	0	..

reheated many times and considerable care taken in hammering. The copper-boron steels should not yet be definitely condemned for their poor forgeability, but experience to date indicates the existence of numerous variables that require further study.

As a result of this manufacturing difficulty, only a limited amount of steel was available for commercial tests, and these tests were not completed in every instance due to the development of another alloy which accomplished the same purpose without boron.

Decarburization—Machined samples of various sizes were subjected to normal heat treating temperatures and decarburization noted by microexamination as well as hardness measurements. Typical results are shown in Table VIII. Data indicate that 0.05 per cent boron with about 2.75 to 3.30 per cent copper is the minimum percentage required to reduce decarburization to an unobjectionable amount. When vanadium was increased to 2.00 per cent the decarburization increased.

General Metallurgical Data—The copper-boron-molybdenum steels have many features in common with the alloys previously referred to. The best hardening temperature was found to be 2150 to

2200 degrees Fahr., the higher temperature being suitable for steels with boron on the low side, and the lower for steels with boron on the high side. After quenching, a Rockwell of 58-60 C was obtained, and after a 1050-degree Fahr. draw this increased to 65-66 C. If heated to 2300 degrees Fahr. or more the steel became "mushy," and if the boron happened to be at 0.15 per cent this characteristic was

Table VIII
Specimens ⅜ Inch and ½ Inch Square

Steel No.	Analysis C	Mn	Si	W	Cr	V	Mo	Cu	B	Decarburization in 0.001 Inch: 1600° 10′ 2200° 2½′ 1000° 2 Hrs. 1% O_2	1500° 10′ 2200° 3′ 1025° 2 Hrs. 6% CO	1500° 10′ 2200° 5′ 1050° 1 Hr. Neutral	1500° 10′ 2200° 2′ 1050° 2 Hrs. 1% O_2	1500° 10′ 2150° 3′ 1050° 2 Hrs.
1	0.80	0.30	0.30	1.50	4.00	1.10	8.75	....	....	0.007	0.003	0.0065	0.005	0.006
2	0.72	0.57	0.25	1.87	4.01	1.04	8.67	2.70	0.02	.....	.....	0.0015	.....	.....
3	0.85	0.52	0.25	1.55	3.94	1.08	8.40	2.86	0.04	.....	.....	.....	trace	.....
4	0.72	0.28	0.29	1.51	3.38	2.14	8.23	....	0.05	.....	.....	.....	0.004	.....
5	0.83	0.56	0.27	1.88	4.01	1.23	7.82	3.32	0.05	trace	.....	.....	.....	.....
6	0.83	0.61	0.33	1.79	4.25	1.24	9.00	3.52	0.07	trace	.....	.....	.....	.....
7	0.89	0.52	0.20	....	3.87	1.64	9.24	2.94	0.07	.....	trace	.....	.....	.....
8	0.80	0.26	0.21	1.81	4.30	1.18	8.80	2.84	0.142	.....	.....	.....	.....	0.0005
9	0.78	0.31	0.22	1.77	4.30	2.16	8.90	2.92	0.166	.....	.....	.....	.....	0.001

noticed even at temperatures as low as 2150 to 2200 degrees Fahr. In heat treating, the fracture coarsened at 50 to 100 degrees Fahr. lower than a molybdenum-tungsten steel without boron and copper. The temperature at which a eutectic developed was the same for the copper-boron as for the straight boron steels. The microstructure of a properly hardened sample is very similar to the structure of hardened molybdenum-tungsten steel. Fig. 3 shows the hardness obtained after various heat treatments.

Cutting Tests—A number of laboratory lathe and drill cutting tests were made and the average indicates that the copper-boron steels are at least equal to the molybdenum-tungsten type. There is nothing to indicate that they have an advantage, although in several tests phenomenal results were obtained. Typical accelerated lathe breakdown tests are reported in Tables IX and X.

Due to the smaller amount of boron necessary, copper-boron steels had a slight advantage in forgeability over the straight boron materials. This improvement, however, was not sufficient to make the steel practical from a manufacturing standpoint. The only advantage of the copper-boron-molybdenum steels over existing types would be reduced decarburization. The disadvantages would be:

(1) Poor forgeability.

(2) Cost of copper and boron.

(3) Presence of copper in scrap that might be used when melting molybdenum-tungsten steel for customers having a limiting copper content in their specification.

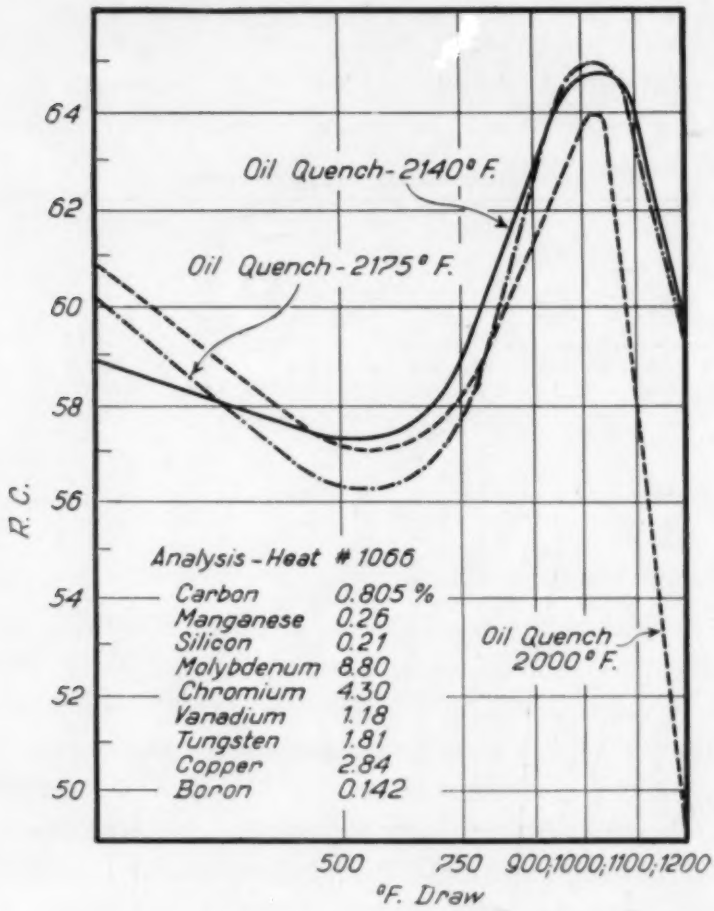


Fig. 3—Hardness Curves Obtained After Various Heat Treatments.

Steel No. 4

Approximate Analysis

6.00 Per Cent Tungsten, 6.00 Per Cent Molybdenum, 1.50 Per Cent Vanadium, 4.00 Per Cent Chromium, 2.50 Per Cent Copper

Since the experiment with boron-containing steels had been discouraging, investigations were continued using copper and omitting boron. Previous work indicated that with copper alone some change in analysis would be required, and after much experimenting an alloy of the following composition was decided upon: Carbon 0.75 to 0.80, manganese 0.25 to 0.40, silicon 0.20 to 0.40, chromium 3.75 to 4.25,

molybdenum 5.75 to 6.25, tungsten 5.75 to 6.25, vanadium 1.40 to 1.60, copper 2.50 to 2.70. Limited experience to date indicates good forgeability at a temperature of about 2100 degrees Fahr. The ingots or billets do not have to be coated with borax at forging or rolling operations.

Table IX
Accelerated Lathe Breakdown Test
Spindle Speed 364 RPM—Feed 0.006 Inch—Depth of Cut 0.030 Inch
Tools ⅜ Inch Square—Started at Center of Disk and Moved toward Periphery

Steel No.	C	Mn	Si	W	Cr	V	Mo	Cu	B	Maximum Surface Feet Cut Before Failure	Rockwell C
Mo-W	0.75	0.33	0.17	1.78	4.41	1.29	8.67	....	.....	324	64.9
1066	0.80	0.26	0.21	1.81	4.30	1.18	8.80	2.84	0.142	301	64.8
1053	0.78	0.30	0.30	1.75	4.25	1.25	8.50	2.90	0.15	327	65.4
1065	0.78	0.31	0.22	1.77	4.30	2.16	8.90	2.92	0.166	319	64.5

Table X
Lathe Breakdown Test
Speed 120 SFPM—Depth ⅛ Inch—Feed 0.037 Inch
Cutting S.A.E. 2335 of 213/220 Brinell—Soluble Oil Coolant

Steel No.	C	W	Cr	V	Mo	Cu	B	Rockwell C	Minutes Run
50075	0.84	1.39	3.61	1.50	9.62	....	....	66.5	16′ 12″
50216	0.79	....	4.31	1.60	9.01	2.93	0.14	64.0	18′ 48″

Fig. 4 shows the microstructure of an annealed sample, Brinell 228. The best heat treatment consists of quenching from 2200 to 2250 degrees Fahr., although for some types of lathe tools 2325 degrees Fahr. has been used to advantage. Table XI shows the hardness obtained at various quenching and drawing temperatures. Figs. 5 and 6 show hardened and drawn structures at magnifications of 500 and 1500, respectively.

Cutting Tests—Laboratory lathe breakdown tests indicate that this steel cuts as well as the best of the molybdenum steels on the market. Outside commercial tests have not been so conclusive. Some reports show better, and some results are worse than the molybdenum-tungsten steels now being used. As yet there are insufficient cutting data to attempt any classification.

Decarburization—Compared with the regular molybdenum-tungsten or molybdenum-vanadium steel, this material represents a marked improvement. For example, machined samples heated to 2200 degrees Fahr. for 10 minutes in an oxidizing atmosphere show less than 0.004-inch soft surface, while the regular molybdenum-tungsten or molybdenum-vanadium steels show 0.012 to 0.013 inch.

Table XI

Hardening Series for
6.0 Per Cent Tungsten, 6.0 Per Cent Molybdenum, 2.5 Per Cent Copper Steel

Samples were turned down to ⅞ inch round, and a ⅛ inch wide flat surface planed off on opposite sides for hardness determinations. Specimens were cut 2½ inches long. They were preheated at 1600 degrees Fahr. for 15 minutes, held at high heat temperatures indicated below for 4 minutes, and oil quenched. All were hardened in a gas, atmosphere controlled furnace.

Test No.	Temperature Degrees Fahr.	Rockwell C	Fracture
1	1900	57.5-58.5	Quite refined
2	2000	61-62	Quite refined
3	2050	62-62.5	Quite refined
4	2100	62.5-63	Refined
5	2150	62-63	Refined
6	2200	62-63	Refined
7	2250	61.5-62.5	Slightly coarse
8	2300	60-61.5	Quite coarse

Note: Hardening range 2200 to 2250 degrees Fahr., oil quench

Drawing Series

Specimens of same size and length as used in the hardening series were preheated at 1600 degrees Fahr. for 15 minutes, held 4 minutes at the high temperature of 2225 degrees Fahr., and then quenched in oil. Tempering time was 2 hours, in an electric circulating air furnace.

Test No.	Temperature Degrees Fahr.	Rockwell C
17	As quenched	62-63
18	400	59-60.5
19	500	59-60
20	700	60-61
21	900	64-65
22	950	65-66
23	1000	65-66
24	1050	65-66
25	1100	64.5-64.5
26	1200	57-58

No decarburization

Conclusions

This type of steel is still in the process of development and test, and it is too early to attempt an appraisal. It is indicated that from a manufacturing standpoint this analysis would be satisfactory and have the advantage of not requiring any coating when heated for cogging or rolling. Considering decarburization, it is a definite improvement over existing molybdenum high speed steels. Disadvantages would be higher alloy cost and presence of copper in scrap, as previously explained under Steel No. 3.

Steel No. 5

4.00 to 6.00 Per Cent Tungsten, 3.50 to 6.00 Per Cent Molybdenum, 4.00 Per Cent Chromium, 1.00 to 1.60 Per Cent Vanadium

Another more recent steel now in process of development and test, and which shows considerable promise, has the following analysis

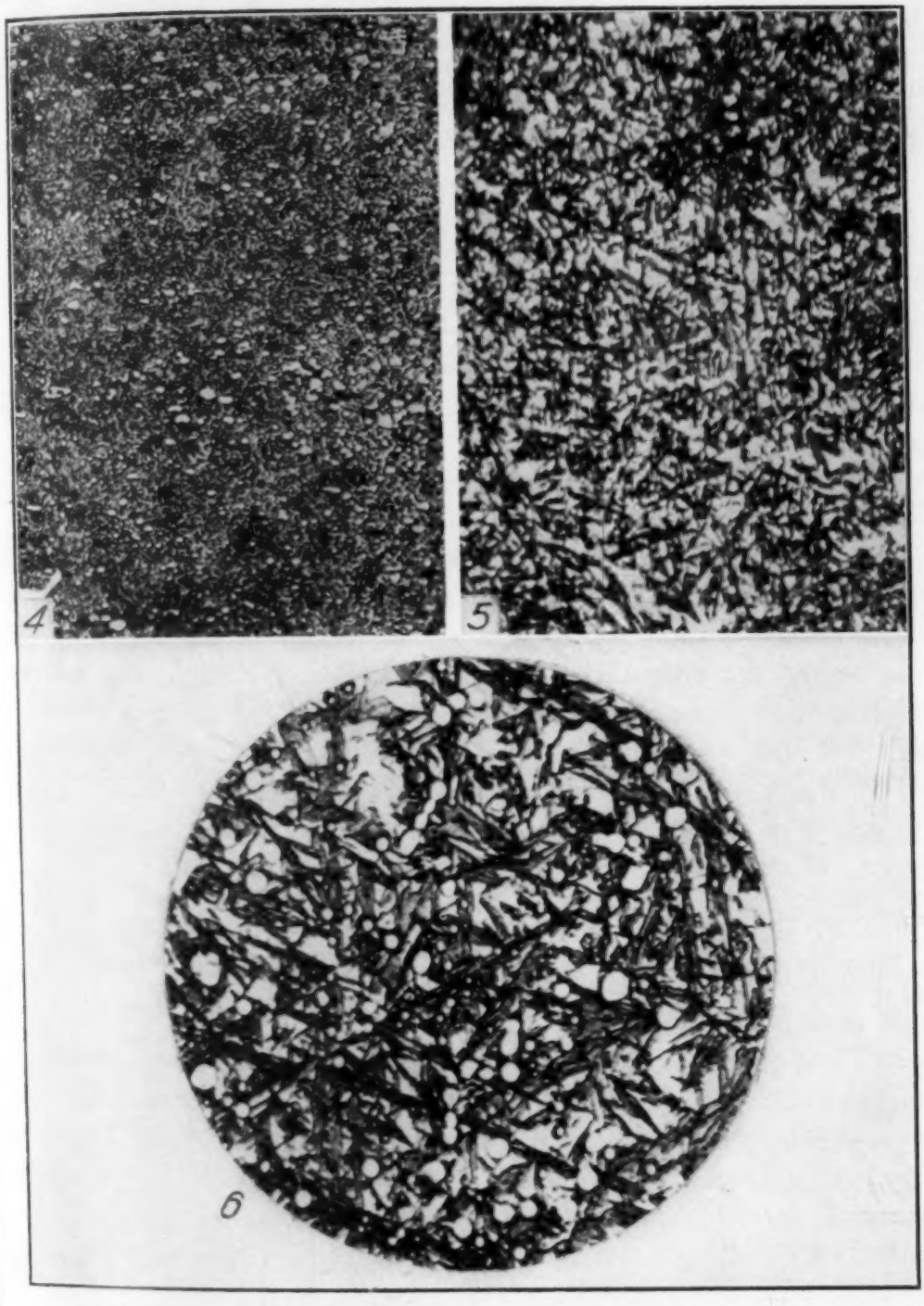


Fig. 4—Microstructure of Annealed 1-Inch Round Bar-Steel No. 4. Etchant 2 Per Cent HNO_3 in Water. × 500.

Fig. 5—Quenched in Oil from 2225 Degrees Fahr. Tempered 2 Hours at 1050 Degrees Fahr. Rockwell C 65.3, Etched 10 Per Cent Nital. × 500.

Fig. 6—Same as Fig. 5. Etched 10 Per Cent Nital. × 1500.

range: Carbon 0.75 to 0.85, manganese 0.20 to 0.40, silicon 0.30 to 0.80, chromium 3.50 to 4.50, molybdenum 3.50 to 6.00, tungsten 4.00

to 6.00, vanadium 1.00 to 1.60. This composition works very well in the mill and does not require borax or any coating in the heating operations. It anneals to about 228 Brinell and in this condition machines satisfactorily. The best hardening temperature has been found to be between 2275 and 2325 degrees Fahr., and when hardened in an ordinary semi-muffle gas furnace without a coating of borax, the parts come out clean of scale and have a file hard surface. Rockwell readings taken on the surface after hardening average 63-65 C. Satisfactory performance has been obtained with tools tempered at 1025 to 1125 degrees Fahr., and the hardness on the surface and in the interior after tempering, averages 64-67 C and a file hard condition is maintained.

One interesting observation regarding this analysis is that practically all the carbides go into solution when heated for hardening. This means that the matrix receives the benefit of nearly all the tungsten, molybdenum and vanadium in the steel. In prolonged decarburization tests in oxidizing atmospheres, the steel does not decarburize any more than 18-4-1. Lathe and drill cutting tests to date indicate performance equal to 18-4-1 or better. A steel of this type has low alloy and over-all cost, and there are no objectionable alloys from the scrap standpoint. The analysis appears to have definite merit but no worthwhile appraisal can be made until a great many more cutting tests have been reported.

Summary

Considering cost, performance, and physical properties, the molybdenum-tungsten type has not yet been surpassed as a general purpose molybdenum high speed steel. The molybdenum-vanadium steel has a greater tendency to decarburize and it is too early to rate general performance. For several types of tools, it has proven very satisfactory. The boron and copper-boron steels (No. 2 and No. 3) have definite manufacturing disadvantages. Steels No. 4 and No. 5 are in process of testing and no definite conclusions can be reached as yet. Of these two, No. 5 steel appears to have the advantage due to the absence of copper and slightly lower alloy content.

The following acknowledgments are made:

(1) To Mr. Gorham of the Gorham Tool Company, Detroit, for valuable information on the boron steels.

(2) To the Climax Molybdenum Company, Detroit, for valuable information on the copper-boron and 6.00 per cent molybdenum, 6.00 per cent tungsten and 2.50 per cent copper steels.

(3) To F. B. Lounsberry, Vice-President, Allegheny Ludlum Steel Corporation, for helpful suggestions and permission to publish this information.

(4) To R. P. De Vries, Director of Research, Allegheny Ludlum Steel Corporation, for suggestions and data on Steel No. 5.

(5) To W. H. Wills, Metallurgist, Allegheny Ludlum Steel Corporation, for helpful suggestions.

DISCUSSION

Written Discussion: By J. H. McCadie, metallurgist, National Twist Drill and Tool Co., Detroit.

The author has given an excellent contribution covering the merits and some of the difficulties encountered in the manufacture and use of molybdenum high speed steels. In general I agree closely with the results stated in the paper.

I am particularly interested in steel No. 5 because it gives promise of eliminating most of the difficulties encountered in the use of the older types of molybdenum steel. I have had the privilege of experimenting with a small quantity of this steel and have found that it can be heated and worked both in forging and hardening with the equipment at hand without the necessity of guarding against decarburization, by covering with borax or other protective practices.

In the hope of helping in the development of a steel more resistant to decarburization than the present molybdenum steel, I am offering the data in the tables accompanying the present discussion.

The specimens were 3 inches long, cut from 0.203-diameter ground drill rod and tested without further machining. They were hardened in a controlled atmosphere furnace. Tempering was done in a circulating hot air type furnace. All specimens were quenched in oil from the hardening heat. The times given are the actual times the specimens were in the high heat furnace and do not include the preheating, which was done in another furnace held at 1500 degrees Fahr. The loads given were those required to break the specimens when supported on knife edges 2½ inches apart, with the load applied at the center.

The grain size was obtained by magnifying the polished and etched specimen, in the as-quenched condition, to 1000 diameters and counting the grains intersecting a 5-inch line.

It was estimated that the specimens reached the temperature of the high heat furnace in approximately 40 seconds.

All Specimens Tempered Two Hours 1025 Degrees Fahr.

Temperature Degrees Fahr.	Time Seconds	Rockwell "C"	Load in Lbs.	Grain Size
2100	40	59.7	900	No Grain
2150	40	61.9	993	No Grain
2200	40	63.4	787	23
2225	40	64.1	735	21
2250	40	65.2	693	16
2275	40	65.4	637	14
2300	40	66.4	656	10
2325	40	66.5	611	10
2200	30	61.5	892	No Grain
2225	30	64.0	768	23
2250	30	64.4	772	21
2275	30	65.0	738	17
2300	30	65.2	731	13
2200	90	65.9	562	18
2225	90	66.0	555	18
2250	90	66.4	588	12
2275	90	66.9	487	7
2300	90	67.0	412	6

Hardening Temperature 2320 Degrees Fahr.—40 Seconds

Tempering Temperature Degrees Fahr. 2 Hours	Rockwell "C"	Load in Lbs.	Grain Size
1000	66.4	588	10
1025	66.1	581	10
1050	65.5	653	10
1075	65.1	675	10
1100	63.8	731	10
1125	63.4	712	10

Hardening Temperature 2225 Degrees Fahr.—40 Seconds

Tempering Temperature Degrees Fahr. 2 Hours	Rockwell "C"	Load in Lbs.	Grain Size
1000	65.3	693	17½
1025	64.4	776	17½
1050	63.5	768	17½
1075	62.2	956	17½
1100	61.5	1038	17½
1125	61.0	956	17½

The results shown in the first table would indicate that the steel has a fairly wide hardening range. Good strength and hardness with a fine grain are obtained at from 2225 to 2250 degrees Fahr. The steel seems to have the property of dissolving the carbides very rapidly at the hardening heats. This we think is the cause of the loss of strength and increase in the grain size at the higher temperatures and longer times.

The second and third tables show that the steel has good red hardness and responds to tempering in a very desirable manner.

It is hoped that Mr. Breeler will give us more information regarding this steel very soon.

Written Discussion: By P. A. E. Armstrong, Latrobe Electric Steel Co., New York.

I have carefully read the author's paper with a great deal of interest, and I know molybdenum high speed steels are capable of being improved by departing from the present usual analysis.

Tungsten is a useful addition. It should be used to replace some of the molybdenum, and if 8 per cent or more of molybdenum is employed, it requires higher chromium than 3.5-4 per cent to bring out the full effects of the various elements for superior cutting efficiency and protection against decarburization.

Whatever merits boron has, it certainly does not make for ready forging or rolling.

Steel No. 5 is very interesting as this is embraced in my work that I did prior to 1922 and subsequently. The analysis is covered within the scope of my patent No. 1,496,980 issued in 1924. I have obtained greater cutting efficiency out of steels within the range given for No. 5 than can be obtained from the more usual and well-known high speed steels of the 18-4-1 type. Cobalt makes a very efficient addition. A very excellent high speed steel, however, can be produced without the cobalt addition.

A contemporary steel to the No. 5 analysis was the very excellent steel that was used for Cleveland Twist Drill Company's Mezzo drills. This was a very balanced alloy and, considering the small amount of alloy present, it did remarkable work.

My experience with steels of the type of the author's No. 5 has shown that chromium should be somewhat in excess of 4 per cent, the molybdenum and tungsten about the same or somewhat higher, the relationship between these and Mezzo steel, and its modifications, being similar.

The vanadium is advantageous if it is kept in the neighborhood of 2 per cent rather than 1 per cent. High vanadium must be compensated for by increased carbon, therefore where the carbon is about 0.80 per cent, the vanadium is better about 1.75 per cent.

Written Discussion: By R. P. DeVries, director of research, Allegheny Ludlum Steel Corp., Watervliet, N. Y.

We wish to record our appreciation of the assembly in one paper of some of the recent developments in the field of high speed steel. The attempt to appraise their value has been enhanced by the many practical considerations dealt with, such as forgeability, tendency to decarburize and contamination of scrap with normally undesirable elements. All of these are essential items of immediate consideration to both producer and consumer.

High speed steel development after the initial work done by Taylor in the early 1900's was summarized by him almost 20 years later as having made no signal advance over his early work. Breeler's paper records some of the outstanding developments made 30 years after the time of Taylor's initial work. All of the steels here dealt with have roughly only one half of the total high melting point elements of the standard 18-4-1 type analysis. The paper attests to the fact that these steels containing less alloy content with molybdenum always present are, from the standpoint of both the manufacturer and the user, much more critical in their behavior than the standard 18-4-1 type. It may be noted that most of the steels discussed employ both tungsten and molybdenum and that when the element tungsten is omitted, the tool efficiency has been stepped up by increased use of higher vanadium contents. Boron

and other elements have been used in combination to overcome some of the natural obstacles.

The research department of the Ludlum Steel Company laid the basis for this type of work in the years 1923 and 1924, which work is embodied in the patent No. 1,496,980 issued to Mr. Armstrong as far back as the year 1924. With the advent of the Emmons type of high speed steel and the development of sintered carbides for use as cutting tools, this initial work was reviewed with the result that after three years of intermittent investigation the steel No. 5 of Breeler's paper was developed as having outstanding possibilities in the low alloy range of high speed steels. The space that Mr. Breeler could devote to this steel is, we hope, no index of the importance of this "new comer" to the field. A few additional observations may therefore be of interest to the many users of high speed steel both in outlining the possibilities that exist in this field as well as in emphasizing the critical nature of these steels when they are seriously considered for actual replacement of much more expensive grades.

The analysis which is roughly defined in the paper under discussion as 4 to 6 per cent tungsten, 3.5 to 6 per cent molybdenum, 4 per cent chromium and 1 to 1.60 per cent vanadium, must in actuality be much more closely defined for best results in actual practice. The first consideration of the investigation could not be one of cost but the production of an alloy suitable to replace existing types of steels with at least an equal or higher type of cutting efficiency. After quite a few trials it was found that the quantity of expensive alloys used was no criterion of the efficiency of the steel obtained. It was, however, disclosed that definite ratios of molybdenum to tungsten not exceeding, in general, a well defined maximum of 9 per cent tungsten and molybdenum combined were found to give results that could not be obtained by the use of slightly greater quantities or much greater quantities of both these elements in combination.

The next consideration was to establish whether steels well balanced as to their main constituents were more or less critical in other aspects. Breeler has dealt briefly but adequately with the manufacturing phases that are paramount, not only in the manufacture of the steel but also the manufacture of tools from the steel. These factors are briefly: freedom from forging difficulties, freedom from decarburization without the use of protective coatings, good machinability of annealed structure, as well as good tool efficiency over a wide range of applications. It must be considered rather noteworthy that all of these requirements can be obtained as fully as they are existent in the best standard types of steels and still be accomplished with low alloy-contained cost. It is, incidentally, a rather disparaging comment on the state of our knowledge with regard to the alloying of elements for practical and useful considerations, for in the investigation referred to, many combinations of elements, costing considerably more than the Steel No. 5, showed very poor efficiency indeed, when tested in tool applications.

Extensive cutting tests of various steels have been run intermittently over a period of two years to establish the cutting efficiency and operating characteristics in tool service. After the completion of many preliminary tests, two steels coming within the scope of the analysis referred to by Breeler as

Steel No. 5 were selected for still more extensive tests. Steel No. 282 and No. 283 were melted to the following analysis:

Type Analysis

	Steel 282	Steel 283
Carbon	0.75-0.80	0.78-0.84
Chromium	3.50-4.00	3.75-4.25
Silicon	0.55-0.90	0.20-0.35
Manganese	0.60-0.90	0.20-0.35
Molybdenum	3.30-4.00	5.50-6.00
Tungsten	4.60-5.00	5.50-6.00
Vanadium	1.40-1.60	0.90-1.10

This range of analyses shows none of the disadvantages in manufacturing of steel or tools discussed by Breeler.

It will be noted that as far as the molybdenum and tungsten contents are concerned, the Steel No. 282 represents the lower end of the range noted under Breeler's general analysis range for Steel No. 5, and Steel No. 283 represents the upper portion of this range. The slight differences in silicon and vanadium content are adjusted to the requirements of the two steels on an experimental basis.

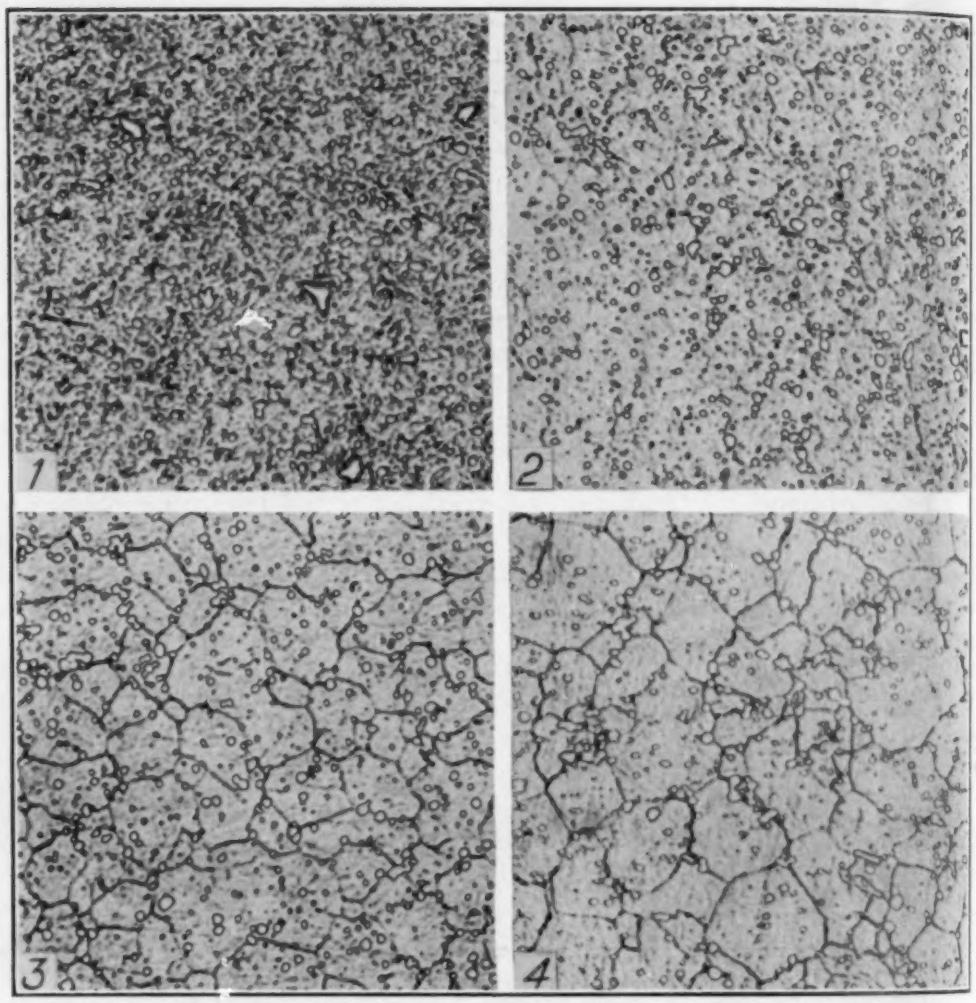
These steels were always tested against a standard 18-4-1 high speed steel and in some tests against a steel of the general specification of: carbon 0.72 to 0.81 per cent, silicon 0.20 to 0.45 per cent, manganese 0.30 per cent maximum, chromium 3.50 to 4.00 per cent, tungsten 1.30 to 1.80 per cent, vanadium 0.90 to 1.30 per cent and molybdenum 8 to 9.50 per cent hereinafter identified as 8-4-1.

Summary of Lathe and Drill Tests
Performance Given in Per Cent

No.	Type	Steel 282	Steel 283	Standard 18-4-1	8-4-1	Lubricant
1	Lathe	100	78	65	58	no
2	Lathe	100	98	98	78	yes
3	Drill	100	81	92	67	yes
4	Drill	100	80	89	..	yes

The tests reported in the table above are not given in detail and not with the objective of emphasizing the superiority established in these tests, but rather to call attention by comparison to a few interesting matters. All of the cutting tests are given merely on a percentage basis.

All of the tests shown in the table rate the performance of Steel No. 282 as 100 per cent and relate the performance of the other steels to them on a percentage basis. The technique of all these tests was the same. Lathe tools and twist drills were accurately ground. Every condition of test which could be controlled was accurately controlled. Two regrinds and sometimes four were taken for one lathe tool or twist drill test. Clearance angles, grinding and regrinding were done with machine tool precision. Variability in the machining quality of the logs under test is probably one of the greatest vari-



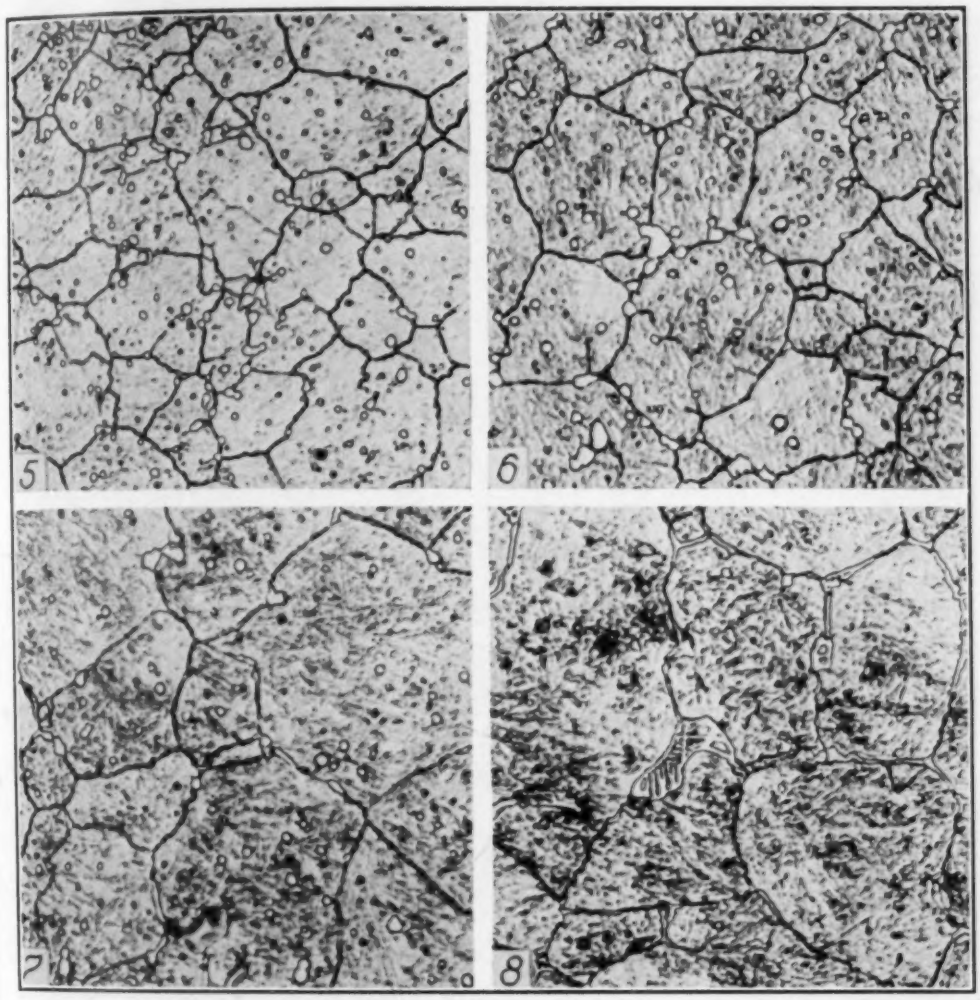
Figs. 1 to 4—Photomicrographs of Steel 282. Size ¾ Inch Round, × 500. Etchant, 10 Per Cent Hydrochloric Acid, Sp.G. 1.18, 3 Per Cent Nitric Acid, Sp.G. 1.42, 87 Per Cent Methyl Alcohol, Absolute. 2 Minutes.

Fig.	Designation	State
1	No. 1 Plain	2000 Degrees Fahr. Oil—Not Tempered
2	No. 2 Plain	2100 Degrees Fahr. Oil—Not Tempered
3	No. 3 Plain	2200 Degrees Fahr. Oil—Not Tempered
4	No. 4 Plain	2250 Degrees Fahr. Oil—Not Tempered

ables encountered. Every precaution was taken to eliminate the factors of variability as expressed in terms of differences in machinability of the steel used for testing the tools.

The first lathe tests were run entirely without any coolant or any lubricant with the result that the nose of the tool for the greater portion of the test was well in the zone of the temperatures through which the tools were tempered after hardening, namely 1025 degrees Fahr. The percentage results represent the average of all the heat treatments used and all of the regrinds made on the various tools.

The second set of lathe tests was run on S. A. E. 2335 log heat treated to an average of 210 to 225 Brinell. The log was 9 inches in diameter, 12 feet in length, driven by a 100 H.P. motor taking ¼ inch depth of cut at a

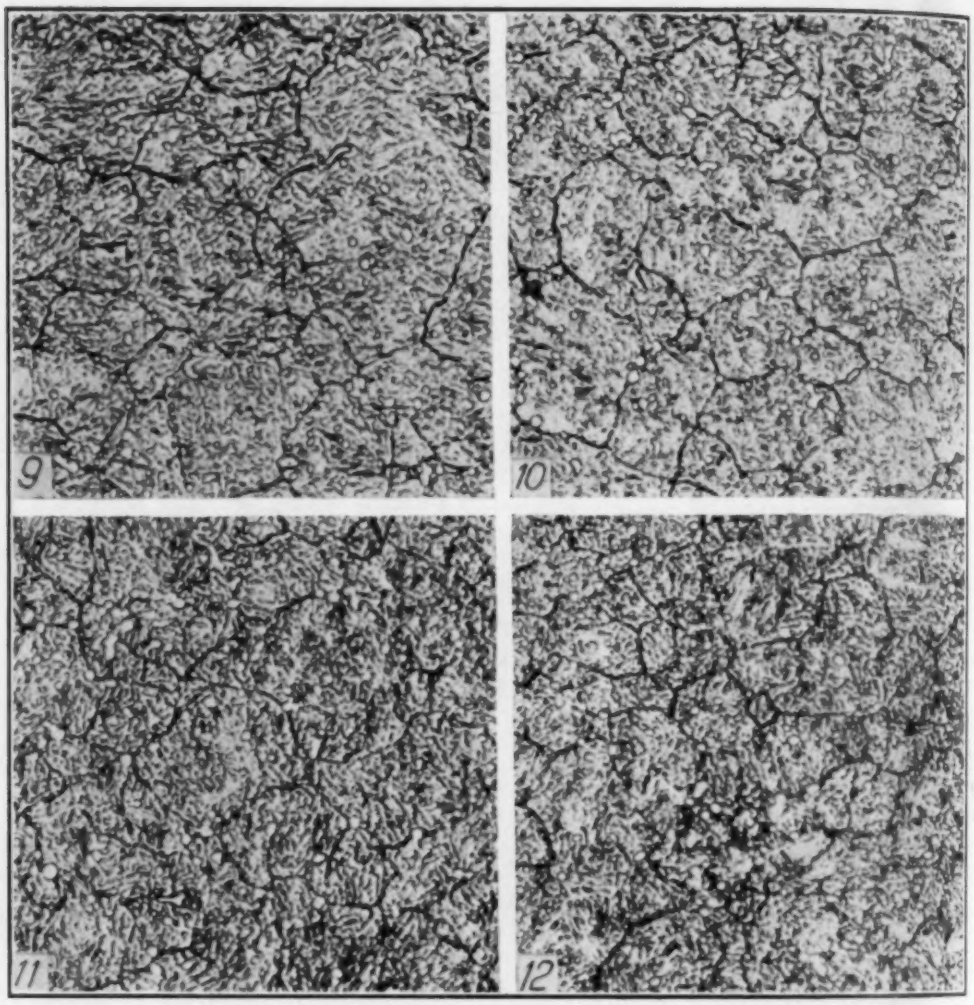


Figs. 5 to 8—Photomicrographs of Steel 282. Size ⅞ Inch Round. Etchant, 10 Per Cent Hydrochloric Acid, Sp.G. 1.18, 3 Per Cent Nitric Acid, Sp.G. 1.42, 87 Per Cent Methyl Alcohol Absolute. × 500. Figs. 5 and 6—2 Minutes; Figs. 7 and 8—3 Minutes.

Fig.	Designation	State
5	No. 5 Plain	2300 Degrees Fahr. Oil—Not Tempered
6	No. 6 Plain	2325 Degrees Fahr. Oil—Not Tempered
7	No. 7 Plain	2350 Degrees Fahr. Oil—Not Tempered
8	No. 8 Plain	2375 Degrees Fahr. Oil—Not Tempered

0.032 feed. A variable speed D.C. motor maintained the surface feet per minute constant at any speed that was desired. The second set of lathe tests shows that the difference between the respective tools under test was less pronounced. The outstanding difference between the second lathe test and the first one given previously is that the tools in the second lathe test were cooled with a powerful stream of lubricating coolant. The coolant was so effective that at the end of the test when the tool had failed, the nose of the tool was not more than hand warm.

The next extensive test was made on drills 1 inch, $\frac{7}{16}$ inch and $\frac{3}{16}$ inch in diameter, and the averages reported in Drill Test No. 3 above show the averages as compiled from all tools with various ranges of heat treatments. Speeds and feeds were well into the upper range of commercial production of

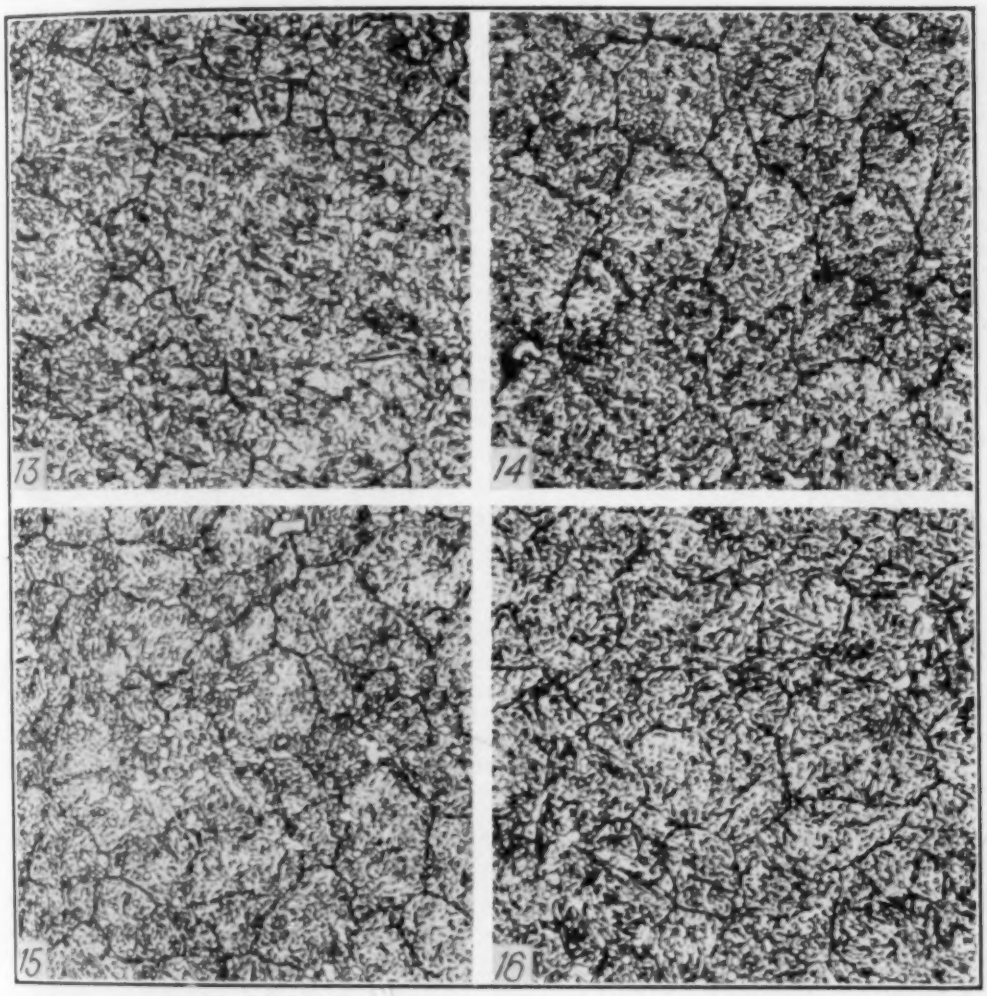


Figs. 9 to 12—Photomicrographs of Steel 282. Size ⅞ Inch Round, × 500. Etchant, 10 Per Cent Hydrochloric Acid, Sp.G. 1.18, 3 Per Cent Nitric Acid, Sp.G. 1.42, 87 Per Cent Methyl Alcohol, Absolute. Fig. 9—3 Minutes; Fig. 10—2½ Minutes; Figs. 11 and 12—2 Minutes.

Fig.	Designation	State
9	No. 2 Nicked	2300 Degrees Fahr. Oil—Tempered 400 Degrees Fahr.
10	No. 3 Nicked	2300 Degrees Fahr. Oil—Tempered 500 Degrees Fahr.
11	No. 4 Nicked	2300 Degrees Fahr. Oil—Tempered 600 Degrees Fahr.
12	No. 5 Nicked	2300 Degrees Fahr. Oil—Tempered 700 Degrees Fahr.

speeds and feeds. All tests were run with lubricant and coolant. Comparing tests 1, 2 and 3, the Steel No. 282 shows certain superiority which is very marked when no coolant is used as in the first test, not so marked when ample coolant is used in the second test, and again very marked in the third and fourth tests where coolant was used. The reason for this may be that the tools made from 282 possess greater red hardness and resistance to wear. That the results of the tests on the twist drills correspond much more closely to the conditions of testing without coolant or lubricant of the first test may simply be an indication that twist drills never get full lubrication and coolant where they most need it, and that is at the point of the drill.

All of the tests on 282 and 283 steel were carried out from at least two

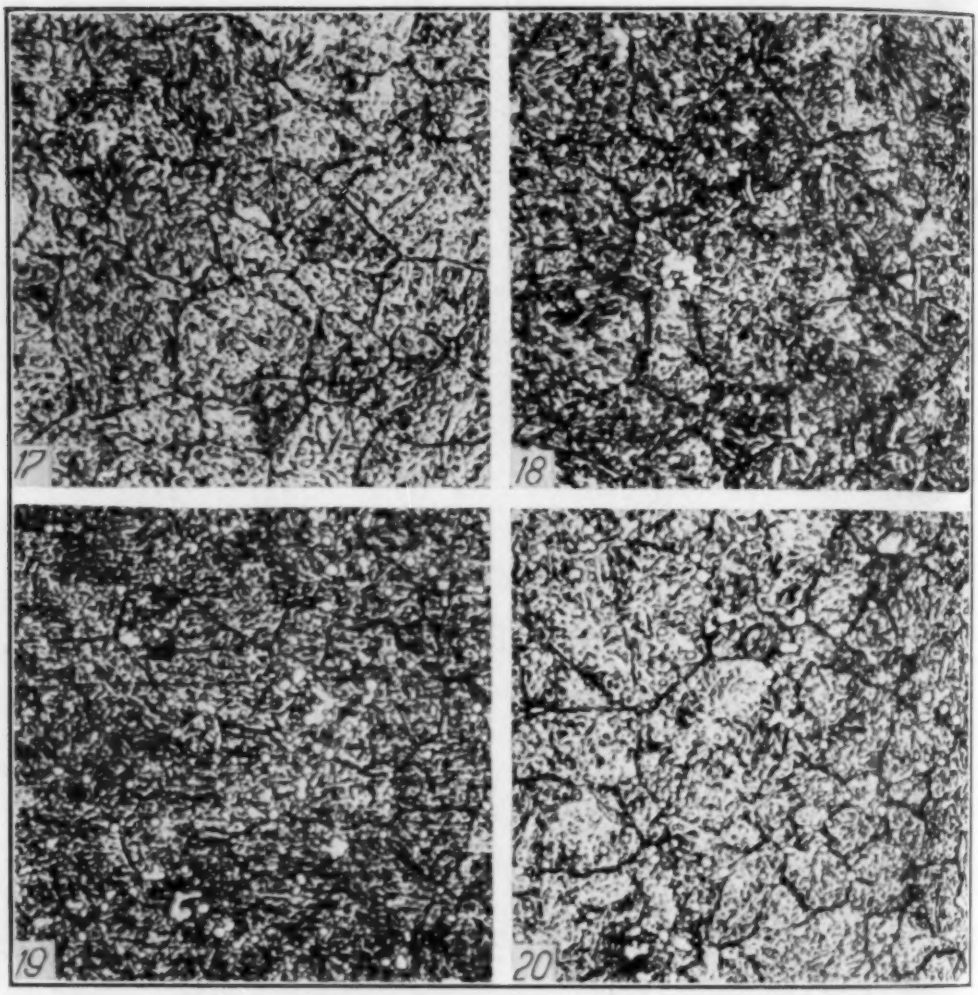


Figs. 13 to 16—Photomicrographs of Steel 282. Size ⅞ Inch Round, × 500. Etchant, 10 Per Cent Hydrochloric Acid, Sp.G. 1.18, 3 Per Cent Nitric Acid, Sp.G. 1.42, 87 Per Cent Methyl Alcohol, Absolute. Fig. 13—1¼ Minutes; Others 1½ Minutes.

Fig.	Designation	State
13	No. 6 Nicked	2300 Degrees Fahr. Oil—Tempered 800 Degrees Fahr.
14	No. 7 Nicked	2300 Degrees Fahr. Oil—Tempered 900 Degrees Fahr.
15	No. 8 Nicked	2300 Degrees Fahr. Oil—Tempered 1000 Degrees Fahr.
16	No. 9 Nicked	2300 Degrees Fahr. Oil—Tempered 1025 Degrees Fahr.

different temperatures of heat treatment, always ranging between 2250 and 2325 degrees Fahr. and tempered to 1025 degrees Fahr. for two hours. In all lathe tests and retests the higher temperatures of heat treatment gave the highest test results but in the case of Steel No. 282, the lowest temperatures at which the tools were heat treated before test gave much better comparative results than the grade that was higher by 3 per cent in tungsten and molybdenum combined.

All steels of 18-4-1 standard analysis and analysis 8-4-1 were heat treated for the cutting tests on the basis of what past experience had shown to bring out the best results. Steels 282 and 283 were always heat treated as aforesaid from two different ranges of temperature and therefore the averages as reported include the results of inferior as well as better heat treatments.



Figs. 17 to 20—Photomicrographs of Steel 282. Size ⅞ Inch Round, × 500. Etchant, 10 Per Cent Hydrochloric Acid, Sp.G. 1.18, 3 Per Cent Nitric Acid, Sp.G. 1.42, 87 Per Cent Methyl Alcohol Absolute. 1½ Minutes.

Fig.	Designation	State
17	No. 10 Nicked	2300 Degrees Fahr. Oil—Tempered 1050 Degrees Fahr.
18	No. 11 Nicked	2300 Degrees Fahr. Oil—Tempered 1075 Degrees Fahr.
19	No. 12 Nicked	2300 Degrees Fahr. Oil—Tempered 1100 Degrees Fahr.
20	No. 13 Nicked	2300 Degrees Fahr. Oil—Tempered 1200 Degrees Fahr.

The microstructure that can be obtained in hardening on steel of Breeler's general analysis range No. 5, correspond very closely to those obtained on Steel No. 282. Photomicrographs 1 to 8 show the steels oil-quenched through a range of temperature from 2000 to 2375 degrees Fahr., by varying degree steps. Photomicrographs 9 to 20 show the structure of the steel as hardened at 2300 degrees Fahr., oil quench and drawn to various temperatures starting with 400 degrees Fahr. and running through to 1200 degrees Fahr., by varying degree steps. The photomicrographs clearly indicate that the range of acceptable hardened structures is defined closely by the temperature range of 2200-2325 degrees Fahr. Where facilities are lacking for close temperature control, even the higher temperatures shown here of 2350 degrees Fahr. will not be destructive of high cutting efficiency for lathe and planer tools.

This discussion has endeavored to show the possibilities that exist of obtaining still greater efficiency in the low alloy content range of high speed steels when due regard is given to all factors which are always encountered in the manufacture and use of the same. We consider it fortunate that this result can be apparently well attained without the use of elements such as copper, boron and other elements which introduce other factors which may partially eliminate certain difficulties while introducing others just as difficult to control.

Written Discussion: By E. Fetz, research metallurgist, Wilbur B. Driver Co., Newark, N. J.

Supported by a wealth of data, Mr. Breeler presents an interesting picture of recent developments in molybdenum high speed cutting steels. He has briefly referred to earlier contributions in this field. Taylor and White already recognized the possibilities of molybdenum. During the world war, similar conditions prevailed in Germany as in the U. S. A. and strenuous efforts were made with a limited success to replace the 18-4-1 standard high speed steel by molybdenum-base alloys. Lately, experimental work on a large scale has been resumed in German research laboratories along the lines of Mr. Breeler's investigation. While Mr. Breeler disclaims the intention of "comparing molybdenum high speed steels with 18-4-1" it was the very object of investigations by Houdremont and Schrader, Scherer and Beutel Rapatz, Pollack and Holzberger to deal a blow to the traditional high speed steels high in tungsten. The approach was from two directions:

(a) by lowering the tungsten content to about 10-13 per cent alongside a slight increase of molybdenum and vanadium and

(b) by partly or completely replacing tungsten by other alloy additions among which molybdenum plays a conspicuous role.

Experiments along the latter line are partly analogous to Mr. Breeler's work and it may be of interest to present in a nutshell a few findings of abroad.

The first table of the present discussion compares the cutting ability of the 18-4-1 high speed steel (Steel No. 1) with steels in which tungsten has been lowered to less than 6 per cent or completely replaced by varying additions of molybdenum and vanadium. All of the steels contain 4 to 4.5 per cent chromium as it has been found that the cutting ability drops markedly with decreasing chromium contents.

As can be seen, a steel having a nominal analysis of 0.9 per cent carbon, 4 per cent tungsten, 2.3 per cent vanadium and 5 per cent molybdenum (Steel No. 9) materially surpasses 18-4-1. Except for the higher vanadium content, this steel falls into the group of Mr. Breeler's steels described on page 306 and characterized as "a more recent steel now in process of development." It indeed shows "considerable promise" as substantiated by cutting tests made abroad. Reducing the molybdenum content to 4.5 per cent and slightly adjusting vanadium and carbon, the cutting performance has not been impaired. Lowering the molybdenum content to 3 per cent (Steel No. 7) and 1 per cent (Steel No. 10) drastically reduces the cutting ability although not below that of 18-4-1. Molybdenum-free high speed steel (Steel 11) yields a much shorter life. In spite of the substantial increase of tungsten and vanadium, respectively to 6 per cent and 4.5 per cent, these steels hold their edge only

half as long as the 1 per cent molybdenum high speed steel containing as little as 2.3 per cent vanadium. It appears that a certain minimum amount of molybdenum is of paramount significance in low tungsten high speed steels. The increase of vanadium above 3 per cent seems to offer hardly any advantages in this class of high speed steels. Another series of tests in the second table shows the superiority of a 6 per cent tungsten, 2 per cent vanadium, 4 per cent molybdenum steel (Steel No. 16) over high speed steels high in tungsten (Steels Nos. 14 and 15). Experiments with molybdenum high speed steels (about 7 per cent molybdenum) which contain no tungsten, yielded about the same service as the 18-4-1 type if the vanadium content is raised to 4 per cent.

The effect of cobalt in molybdenum high speed steels seems to require some further investigations. Mr. Breeler's study of the effect of boron and copper is of great interest.

The author's paper and the international literature offer an abundance of chemical compositions for molybdenum high speed steels and it appears to be an urgent desideratum at this time to accumulate more testing data for selection of the most favorable compositions. These investigations should not be confined to lathe tests but should be extended to drilling and milling experiments as the relative performance in these applications varies quite often. The publication of the experimental results should include a detailed description of the testing conditions.

The proof has been furnished so far that, with proper heat treatment, the newly developed types of molybdenum high speed steels are not only equal to the old 18-4-1 but partly surpass it as to cutting performance and initial cost. Mr. Breeler's contribution represents a very valuable one.

Lathe Breakdown Tests with Molybdenum High Speed Steels in Comparison with 18-4-1

Steel No.	1	2	3	4	5	6	7	8	9	10	11
Tungsten	18.40	....	....	....	1.96	2.47	3.47	4.22	3.98	5.60	5.89
Molybdenum	0.55	3.95	3.47	3.47	3.40	2.86	3.10	4.26	5.08	1.05	....
Vanadium	0.98	5.68	2.40	2.63	2.80	2.63	2.80	2.85	2.29	2.37	4.52
Carbon	0.75	1.49	0.93	1.12	0.99	0.93	1.01	1.07	0.92	0.81	0.81
Min. run	30	14	23	36	25	36	38	57	57	35	17½

Depth of Cut: 0.118 in.
Feed: 0.036 in.
Cutting Speed: 55 ft./min.
Machined Steel: Plain C steel of 106,400 lbs./sq. in.

Lathe Breakdown Test on Molybdenum High Speed Steel in Comparison with Tungsten High Speed Steel

Steel No.	14	15	16	17
Tungsten	19.22	12.45	5.71	2.12
Molybdenum	0.44	0.78	4.06	7.84
Vanadium	1.62	2.60	2.15	1.17
Carbon	0.74	0.83	0.79	0.73
Min. run	37	47	56	35

Depth of Cut: 0.118 in.
Feed: 0.036 in.
Cutting Speed: 48.8 ft./min.
Machined Steel: Manganese-silicon steel of 121,000 lb./sq. in.

Written Discussion: By J. P. Gill, chief metallurgist, Vanadium-Alloys Steel Co., Latrobe, Pa.

Mr. Breeler is to be highly complimented not only in disclosing much

interesting data but also in making possible the discussion of a subject which has not been any too thoroughly discussed in open meetings.

Certainly all of the tool steel manufacturers who produce large amounts of high speed steel have done and are doing considerable experimental work with molybdenum-base high speed steels. Many data and information have been collected that have not been disclosed.

Mr. Breeler has listed three main reasons for prompting the development work in molybdenum high speed steels but it seems to me that possibly several of the most important reasons were omitted, namely, the efforts to produce a molybdenum high speed steel which does not have the narrow heat treating range of the molybdenum-tungsten type and second, to produce a molybdenum high speed steel that does not show wide variations in physical properties even when heat treated under the best controlled conditions. Two examples may be given to illustrate the necessity for such developments. In a test of 600 tools of the same type made of molybdenum-tungsten steel versus 600 tools made of 18.00 per cent tungsten steel, of the best 20 tools of each lot the molybdenum-tungsten steels actually showed about 5 per cent better cutting efficiency. Of the poorest 20 tools of each lot the tools of 18.00 per cent tungsten high speed steel were three times as good as the poorest tools of the molybdenum-tungsten type. The variation in performance between the best 50 versus the poorest 50 of the tools of the 18.00 per cent tungsten high speed steel was in the vicinity of 20 per cent while the variation in performance between the best 50 of the molybdenum steels versus the poorest 50 was over 100 per cent. It is possibly needless to add that the average performance of all of the molybdenum-tungsten tools versus that of the 18.00 per cent tungsten tools was much inferior. To give a second example, the writer is acquainted with at least one large user of molybdenum-tungsten high speed steel who actually heat treats several pilot tools made of each lot or heat of the steel that is received and varies his heat treatment accordingly, a thing unheard of today by tool makers who use 18.00 per cent tungsten high speed steel.

In reference to the molybdenum-2.00 per cent vanadium high speed steels it does not appear that they were any more anticipated by the work of the Watertown Arsenal than were the molybdenum-tungsten high speed steels. The Watertown Arsenal did considerable experimental work in partial replacement of the molybdenum content with tungsten and their steel number 61 had a chemical composition of 0.74 per cent carbon, 4.19 per cent chromium, 1.26 per cent vanadium, 7.06 per cent molybdenum and 4.44 per cent tungsten, which seems just as much a forerunner of the molybdenum-tungsten steels as the steel mentioned by Mr. Breeler was a forerunner of the molybdenum-vanadium steels.

Mr. Breeler has mentioned one or two cutting tests of the molybdenum-tungsten type versus that of the molybdenum-vanadium type. Since these cutting tests are so brief as to be hardly worth mentioning it might be of interest to the audience that during the past two years we have an accumulated test on drills in sizes varying from ¼ to 1¼ inches in diameter. The steel used in these tools was the molybdenum-vanadium, both type 1 and type 2 as given by Mr. Breeler. The molybdenum-vanadium steel was made by three different manufacturers. The molybdenum-tungsten steel was made by

four different manufacturers. The drills were made and tested by five different drill makers. The tests were conducted both in the laboratory and in the field. The accumulated number of tools in these tests is the large total of 6120. The molybdenum-vanadium steels showed a superiority of 36.1 per cent in tool life over that of a like number of molybdenum-tungsten drills against which they were tested and used. In addition to these drill tests we have accumulated over 250 direct field tests of molybdenum-vanadium steels versus molybdenum-tungsten and in 91 per cent of these tests the molybdenum-vanadium steel has shown a marked superiority in cutting performance. There are hundreds of users of molybdenum-vanadium high speed steels that will question Mr. Breeler's conclusion that the molybdenum-tungsten type has not yet been surpassed as a general purpose molybdenum high speed steel.

I would be interested in knowing more about the manner of conducting the impact tests described by Mr. Breeler, since we have not been able to obtain consistent results with impact tests on hardened high speed steel when the steel is about 61 or 62 Rockwell C or higher in hardness. Our experience has been that specimens of all types of high speed steel treated at the same time often vary 100 per cent in the foot-pounds of absorbed energy. Not only have we been unable to obtain consistent results in our own laboratory but two highly reputable commercial testing laboratories have not been able to obtain consistent results in impact testing of extremely hard high speed steel samples. It would be interesting for Mr. Breeler to state something as to the number of specimens he used and also of the maximum variation in results he obtains between different specimens treated and tested alike.

In reference to decarburization of molybdenum-vanadium steels versus that of the molybdenum-tungsten type, our laboratory has made a number of tests at different times under different heat treating conditions and we have never found a material difference in tendency toward decarburization between the molybdenum-vanadium types and the molybdenum-tungsten types. Reports from users of the two steels who have made similar tests confirm these results. We have followed the procedure of testing for decarburization by tempering the specimens to about 1250 degrees Fahr. in order to only soften them slightly and still not affect the decarburization which has resulted from the hardening procedure. We then sand blast the specimens and clean the surface with emery cloth. Successive cuts are made from the surface of the specimen with a carbide tool, the cuts usually being 0.003 inch in depth. The chips are collected from each cut and the carbon determination made. We have found this procedure far more accurate than microscopic examination, due to the fact that microscopic examination does not always disclose a definite difference in structure when only partial decarburization has resulted and for practical purposes partial decarburization may prove as detrimental to the surface of a tool as almost complete decarburization. When round specimens are used an analysis of the chips gives a highly accurate average of the partial decarburization that has taken place, which cannot be obtained by microscopic examination as decarburization is usually not uniform on high speed steel specimens. Typical of the many comparisons which have been made on comparing decarburization on molybdenum-tungsten high speed steels versus that of the molybdenum-vanadium type is one in which an analysis of the furnace atmos-

phere showed 10 per cent carbon dioxide, 1.8 per cent carbon monoxide with no oxygen. One specimen of each steel was placed in the furnace at the same time. The specimens were held 3 minutes, 5 minutes and 10 minutes. Successive cuts of 0.003 inch each in depth were then made and analyzed for carbon. The original carbon content of the molybdenum-vanadium steel was 0.83 per cent and the molybdenum-tungsten steel was 0.80 per cent. The following table shows the results of the test:

Cuts of 0.003 inch in depth.
Specimens were ¼ inch round, machined from 1 inch round.
Heat treating procedure—preheat 1350 degrees Fahr., high 2210 degrees Fahr.
Tempered at 1250 degrees Fahr. Furnace atmosphere 10.2 per cent CO_2 and 1.5 per cent CO.
No oxygen.

		Carbon Content, Per Cent				
		1st Cut	2nd Cut	3rd Cut	4th Cut	5th Cut
Mo-V	3 min.	0.67	0.81	0.82	....	....
Mo-W	3 min.	0.67	0.77	0.80	....	....
Mo-V	5 min.	0.53	0.70	0.80	0.81	....
Mo-W	5 min.	0.57	0.69	0.75	0.78	....
Mo-V	10 min.	0.33	0.53	0.68	0.74	0.76
Mo-W	10 min.	0.30	0.54	0.65	0.69	0.71

The average of the results given by Mr. Breeler of the decarburization for the two types of steels is not greatly different. Anyway this discussion of decarburization is merely academic, as both steels decarburize to such an extent that their surface must be protected and when the surface of either is protected there is positively no difference in their tendency to decarburize.

I would like to offer further discussion of this interesting subject but feel that if I do so my discussion may become longer than the paper.

Written Discussion: By N. I. Stotz, metallurgical engineer, Universal-Cyclops Steel Corp., Titusville, Pa.

We cannot express too strongly to Mr. Breeler our appreciation for this excellent paper. While some parts of it are already historical it is well to have a concise record in our literature of what has gone on so intensively behind the scenes. In a broad sense our experiences parallel those reported by Mr. Breeler. The first sentence in the summary "considering cost, performance, and physical properties, the molybdenum-tungsten type has not yet been surpassed as a general purpose high speed steel" might go further and say that this type continues to hold the same place in the family of molybdenum steels that 18-4-1 holds in the family of tungsten steels.

In the development of the "super" molybdenum high speed steel of the future our experience to date points definitely toward cobalt as the major additional alloying element. Much interesting work is in progress but detailed results are not yet available.

We are particularly interested in Table I on page 295 giving Izod values for two of the molybdenum-vanadium types and the molybdenum-tungsten type. We view all such tables on so complex an alloy as high speed steel with equal suspicion because so often there is no certain common denominator to serve as a standard of comparison. We note, for instance, that a common high heat of 2200 degrees Fahr. has been used for all three steels. Our experience has been that if a given set of furnace conditions are constant as to time and atmosphere about 20 degrees more temperature is required to fully harden the molybdenum-vanadium type. Therefore, under the conditions of this

comparison we would expect the molybdenum-vanadium type to be somewhat underhardened as compared to the molybdenum-tungsten type. This would react to their advantage in resultant Izods. This is an excellent case to illustrate how the use of the quantitative grain size measurements can give a clew to some more reliable common denominator of comparison. Mr. Breeler has used good judgment in interpreting this table rather broadly.

In the case of Steel No. 3, the molybdenum-tungsten type with copper and boron, our tests showed definitely inferior Izod values, but since this steel seems uncommercial from the forgeability angle, detailed discussion may be of no particular value.

Our interest in Steel No. 4 has always been accompanied by two conflicting viewpoints. The presence of copper seems to be an exacting price to pay for the absence of decarburization. Even if there were no hope of relief by any other method this should still cause concern. However, each year has seen further forward development in both liquid baths and atmosphere control in muffle furnaces. This year is no exception.

On the other hand this combination of tungsten and molybdenum without the copper may offer some interesting cutting results even if some decarburization has to be contended with. It is worthy of further study.

Steel No. 5 is broadly patterned after some of the recent interesting steels described in foreign literature except that the foreign compositions are somewhat more generous in vanadium. It has been quite a surprise to us how nearly many of these low alloy grades approach the cutting efficiency of 18-4-1 although our experience to date does not indicate that they are equal. Many tests show efficiencies of between 85 and 93 per cent. Such steels, however, are intermediate in cost between 18-4-1 and the molybdenum-tungsten types due to the appreciable tungsten content in the newer composition.

Recent literature does not altogether support Mr. Breeler's optimistic view of decarburization on Steel 5. Houdremont and Schrader[1] describe a steel containing essentially 4.5 per cent molybdenum, 5.5 per cent tungsten, and 2.4 per cent vanadium. Decarburization by description and photograph shows considerably deeper than any of the tungsten steels free from molybdenum.

Written Discussion: By Victor Stefanides, metallurgist, Illinois Tool Works and Shakeproof Lock Washer Co., Chicago.

High speed steel is not very often a subject of discussion. At such occasions when the subject is brought up, no effort is made to get to the fundamental principles of what constitutes an ideal cutting tool. We are dealing with the so-called tungsten 18-4-1 as well as molybdenum (8-4-1-1.5) high speed steels, and if one were to send out questionnaires, as to which of the two is a better cutting tool, unquestionably there would be some conflicting opinions as to the merit of one or the other. It is with this idea in mind that the writer will attempt to analyze the fundamental principles of cutting tools of which the high speed steels form the major part.

What constitutes an ideal cutting tool in terms of high speed steel? An

[1]Houdremont and Schrader, "Recent Developments in the Field of High Speed Steels Low in Imported Alloying Elements," *Technische Mitteilungen Krupp*, V. 5, p. 227-239, 1937.

ideal cutting tool is one possessing high shock resisting properties with hard particles imbedded in a tough matrix, inert to moderately high temperatures. The high speed steels, subject in this discussion, answer to the above definition. By the above definition we have opened to discussions the two main constituents in the high speed steels, namely: the hard particles or carbides, and the matrix. High speed steel is an austenitic alloy in the as-quenched state. On tempering the hard carbides precipitate and are imbedded in a tough matrix.

It is hoped that the validity of the statement: "The greater the number of carbide particles and the harder the particles, the greater will the efficiency of such tool be," is conceded. If this statement is accepted then it will be recognized that the greater amount of carbon will be instrumental in creating a greater number of carbides, and the greater the percentage of the hard carbide-forming element present the greater will be the number of the hard carbide particles. In the steel under discussion, we have the carbon and the carbide-forming elements, but shall consider only the tungsten and molybdenum as the principal carbide-forming elements.

In the field of metallurgy there appear to be two schools of thought: one professing the tungsten high speed steels to be superior to the molybdenum high speed steels, and the other school claiming just the opposite. Strange to say that both are correct, but no attempt has been made to explain "why." Before an attempt is made to answer the question "why," let us examine the elements given hereby:

Element	Atomic No.	Closest Approach of Atom	Lattice Constant	Type of Crystal Lattice	Density	Possible Carbide in HS Steel
1. Ta	73	2.84	3.281	B. C. CU	16.6	Ta_2C
W (α)	74	2.7097	3.1583	B. C. CU	19.3	
2. W (β)			5.04	CU		W_2C
3. Mo	42	2.708	3.1401	B. C. CU	10.2	Mo_2C
4. Cb	41	2.840	3.03	B. C. CU	8.4	CbC
5. V	23	2.60	3.011	B. C. CU	5.68	VC
6. Cr (α)	24	2.493	2.878	B. C. CU		
(β)			2.717	HEX. C. P.	6.92	Cr_4C
(γ)			8.717	B. C. CU		Cr_3C_2
7. Fe (α)	26	2.4774	2.86106	B. C. CU		
(β) (800° C.)			2.90	B. C. CU		
(γ) (1100° C.)			3.63	F. C. CU	7.86	Fe_3C
(δ) (1400° C.)			2.93	B. C. CU		
C (diamond)	6	2.06	3.5597	F. C. CU	3.5	
(graphite)		1.42	2.48	HEX.	2.25	
Co (α)	27	2.51	2.514	HEX. C. P.		
(β)			3.554	F. C. CU	8.9	
Ni (α)	28	2.487	2.66	HEX. C. P.	8.9	
(β)			3.517	F. C. CU		
Cu	29	2.84	3.608	F. C. CU	8.92	

In the above table a list of elements usually encountered in high speed steel is given, with their atomic number, closest approach of atoms, lattice constant, type of crystal lattice, density and the possible carbide form. The carbide-forming elements are numbered from 1 to 7 inclusive, while the non-carbide-forming elements are not. The elements are given in sequence so as to designate the prominence of the carbide-forming affinity. The list starts with the element tantalum, and the writer is of the opinion that it has the greatest carbide-forming affinity because of the highest lattice constant and

the highest value of the closest approach of atoms. Though it may have the greatest carbide-forming affinity, it does not necessarily mean that it forms the hardest carbide. This, however, will be discussed later. As we go down the line we observe that the atomic number, the lattice constant and the closest approach of atoms is gradually diminishing and with it the carbide-forming affinity. This means, therefore, that if we select an iron-base alloy with the elements from 1 to 7 present with sufficient carbon to form carbides, the element tantalum will combine with the carbon first and what is left of carbon will be taken up by tungsten and so on down the line until all the carbon present is consumed. If a limited amount of carbon is present as for instance in 18-4-1 high speed steel, the tungsten will take up the major portion or about 0.55 per cent and the balance will be left to satisfy the vanadium and chromium. The chromium, although not having as great an affinity for carbon as the vanadium, due to "mass action" will form some carbides. The "mass action" relative to iron will also be a deciding factor, so that we can expect some carbides of chromium and iron as well as vanadium with some free tungsten. However, if it were not for the "mass action" we could hardly expect any chromium and iron carbide, because of the usual amount of carbon present in the 18-4-1, about 0.55 per cent would be taken up by the tungsten, and the balance of the carbon or 0.20 per cent would be just enough to satisfy the vanadium. However, "mass action" interferes with such state of affairs, resulting in a slight amount of chromium and iron carbide.

The writer has classified the element columbium as No. 4, because of its lattice constant, although its closest approach of atoms is equal to that of tantalum. However, it is anticipated that this number is too high and an additional investigation is desired to check its validity.

It will be observed further that all these carbide-forming elements in the list, when in equilibrium, are characterized by the "body-centered cube" crystal lattice, another desirable property which adds to their carbide-forming affinity.

The more one scrutinizes the above list, the more apparent it becomes that there is a very concise mathematical relation between the atomic number, the closest approach of atoms, lattice constant, the crystal lattice, and the density which determines not only the carbide-forming affinity, but the type of carbide and the hardness of the carbide. It is reasonable to assume that in high carbon-high chromium steels the type of carbide one may expect would be the Cr_3C_2, whereas in the presence of high chromium but only a small amount of carbon the Cr_4C type would predominate. In high speed steels where the affinity of tungsten or molybdenum and vanadium to form carbides is the greatest and only a very small amount of carbon is available for the chromium and even that more or less due to "mass action," we may reasonably conclude that the chromium carbide which exists in high speed steels is of the Cr_4C type. It is a well established fact that in 18 per cent chromium, 8 per cent nickel and 0.07 per cent carbon only the Cr_4C type of carbide exists. In Stellite, 18 per cent tungsten, 27 per cent chromium, 50 per cent cobalt, and 2.75 per cent carbon, all of the tungsten goes into forming W_2C carbide, using up about 0.55 per cent of the total carbon, and the balance of the carbon forms Cr_3C_2 combining with about 14 per cent of the total chromium. The balance, or 13 per cent of the total chromium forms a solid solution with the cobalt in which

the tungsten and the chromium carbides are imbedded. If to the above analysis only a small amount of vanadium is added, vanadium carbides are formed in preference to chromium carbides. The vanadium carbides are readily visible under the microscope. If Stellite with higher cutting efficiency is desired the percentage of tungsten is increased, which increases the amount of W_2C but decreases the amount of Cr_2C_2.

If it is desired to increase the efficiency of high speed steel cutting tools the customary procedure is to increase the amount of tungsten and carbon, or the amount of vanadium and carbon with or without cobalt. On the European continent the practice is to use tungsten as high as 22 per cent, vanadium 2 or 3 per cent, carbon 0.90 to 1.00 per cent and cobalt 8 to 10 per cent. With higher tungsten to increase the tool efficiency it is necessary to have higher carbon to increase the amount of W_2C. By increasing the carbon in a standard 18-4-1, not much is to be gained, because the excess carbon after satisfying the tungsten and vanadium carbide-forming affinity will form Cr_2C_2 or Cr_4C and Fe_3C which have a very doubtful value for high speed cutting.

It is quite obvious why the efficiency of a tool should be enhanced by increasing the carbon and tungsten content. Do we accomplish the same by increasing the carbon and the vanadium content? Many believe that we do, and perhaps they are right in their contention. However, the writer was always skeptical about the value of vanadium carbide in high speed steel, basing his skepticism on the density of vanadium which as given in the table is only 5.66 as against 19.3 of tungsten. Of course, it may be argued that in case of vanadium carbide one atom of vanadium combines with one atom of carbon-forming VC whereas in case of tungsten carbide, there are two atoms of tungsten combining with only one atom of carbon forming W_2C. Vanadium carbide in order to approach the hardness of tungsten carbide would have to combine in ratio 1:3 forming VC_3. The writer in order to prove this theory that the VC was not very useful for high speed cutting purposes proceeded in making an alloy of 12.5 per cent vanadium, 4.25 per cent carbon, and balance iron. On examining this alloy under the microscope an abnormal number of vanadium carbides were observed but there was no evidence of graphite as one may have suspected. The alloy was forged successfully at 2100 degrees Fahr. Quenching the alloy in tool bit form from 2100 to 2400 degrees Fahr. a hardness of 65 to 67 Rockwell C was obtained but only limited solubility of carbides was observed. On quenched and tempered specimens at 1000 degrees Fahr., a hardness of 65 to 67 Rockwell C was obtained, and the cutting efficiency was only 5 per cent of that of high speed steel.

Vanadium in high speed steel has a very important function to perform, and that function is that it becomes a carbon carrier. Its function is somewhat similar to that of the red corpuscles in blood streams, which act as oxygen carriers, depositing the oxygen where it is mostly needed. The analogy is perhaps too far fetched but it serves the purpose to illustrate this point. The chemical reaction with regard to vanadium as a carbon carrier is not understood, but judging from the high powered metallographic investigation it appears that the W_2C and VC form eutectics. With this combination the W_2C approaches the hardness of the WC carbide, hardness of which is just below that of diamond.

The action of columbium is similar to that of vanadium; however, the CbC does not appear to form eutectic with the W_2C, and consequently substitution of vanadium with columbium in high speed steel does not have the beneficial effect the vanadium has.

What has been said about tungsten, carbon and vanadium, applies to molybdenum, where molybdenum is being substituted for tungsten. However, if in the molybdenum type of high speed steel tungsten is present, tungsten will be the first one to form carbides; this will be followed by molybdenum, vanadium and so on down the line.

Having established the carbide-forming affinity of the different elements present in high speed steel the next important consideration is their hardnesses. Hardness is defined as that property which resists deformation. Metals respond to deformation most readily when in an annealed condition which is a state of equilibrium. Once equilibrium is disturbed, either by cold working, heating and quenching, driving other elements in solution which establish themselves at the space lattices, is always accompanied by disturbances to the equilibrium, or shall we say, stressing the lattice parameter which manifests itself in hardness. The hardest element known is carbon in the form of diamond. Diamond is a volcanic product, whereby carbonaceous matter was heated to a very high temperature and quenched suddenly under pressure. Moissan the French scientist proceeded somewhat on the same basis by heating sugar to 4000 degrees Fahr. and quenching it under pressure in ice cold water, producing synthetic diamonds. The hardness of diamond is not understood, but it is possible that at very high temperature it exists in a crystalline form which is in equilibrium at that temperature but on cooling tends to change to a different crystalline form; the cooling rate, however, is so rapid that the change does not occur and the crystalline form is retained which is abnormal to room temperature. This condition destroys equilibrium, sets up tremendous stresses, which are manifested in the great hardness. Carbon in other forms such as charcoal, coke, graphite is not hard, and because it is not hard we may conclude that it is in equilibrium under the existing conditions. Carbon in the allotropic form of f.c.cu. (diamond) has a density of 3.5, whereas its other allotropic form or hexagonal (graphite) has a density of only 2.25. It is a tremendous change from one allotrope to another, and hereby lies the secret of the great hardness of diamonds. Evidently the equilibrium is in a hexagonal crystal lattice, density of which is 2.25, yet due to rapid cooling under pressure it exists in a f.c.cu. crystal lattice, density of which is 3.5.

Everybody is familiar with the well known phenomenon of quenched steel. Steel above the critical range is transformed from b.c.cu. to f.c.cu. in which crystalline form the lattice constant has changed from 2.861 to 3.63 thus enabling it to hold the carbides in solution, or may we say that the carbides have entered the space lattice because of the enlargement of the lattice constant and, as such, the steel is nonmagnetic, density of which is slightly higher. On quenching, however, it tends to revert from f.c.cu. crystalline form back to b.c.cu. crystalline form, but is restricted in doing so because the carbides lag behind in coming out of the space lattice or out of solution. The slower action of the carbides retards the transformation of the f.c.cu. parameter of the gamma ferrite into b.c.cu. of the alpha ferrite which creates unbalanced equilibrium,

resulting in residual stresses and consequently in great hardness. Of course the hardness obtained due to quenching of steel is not only due to the unbalanced equilibrium of ferrite and austenite but slight to expension of the alpha ferrite and submicroscopic carbides which are in the stage of coming out of solution. It is understood that with other elements besides carbon present, the solubility of carbon in iron is reduced. The logic of that is simply this: when other elements are present they enter the space lattice of the iron so that there is less space available for the carbides, and consequently there is only a partial solution of carbides. In presence of silicon or aluminum or both the carbon although low may even graphitize. Some carbides may be too large to be comfortably accommodated in the space lattice, so that it takes either too high a temperature or too long time at high temperature to drive them into the space lattice. Illustration of this is high carbon-high chromium, high speed steels, etc. The lower the atomic weight of an element forming carbide, the more readily they go into solution. If carbides are hard to drive into solution, the resulting austenite is hard to break down. Presence of cobalt in high speed steels takes higher temperature to drive the carbides into solution, because part of the space lattice is occupied by the cobalt, and to break down the resulting austenite, takes a more drastic draw than high speed steel without the cobalt present.

Hardness under some extraordinary condition is not a true expression of resistance to deformation in a sense that no true hardness is obtained on hardness testing instruments. The writer has observed on a number of occasions that on testing tools for hardness when 64-65 or even 66 Rockwell C was obtained, on testing with a file, the corresponding hardness was equivalent only to 61-62 or possibly 63 Rockwell C. Standard test blocks checked the instrument to be in good working condition, so that the difference must have been due to some cause unknown to the writer. Some people do not attach much importance to file hardness, yet on checking tools, on which such differences existed, were always inferior in their cutting performance when compared with tools on which Rockwell and file hardness were the same. On investigating the cause of such an effect, it was disclosed that tools of the molybdenum type acted in that manner when hardened in salt baths. Tools hardened in a muffle type of furnace and quenched to a liquid bath of KCl-Na_2CO_3 at 1100 degrees Fahr. followed by air or oil quench possessed the same type of hardness, though similar tools quenched in oil were satisfactory. Tools treated at 1050 degrees Fahr. for surface hardness in molten salts, rich in cyanide content, and subsequently heat treated in a standard manner also gave similar hardness. However, tools hardened on several occasions in fresh barium chloride give satisfactory results, though its use for heat treating molybdenum type steels is somewhat doubtful, because of its great solubility of iron oxide which would be detrimental.

Microscopic investigation of the tools with the erratic hardnesses did not throw any light on the subject, though it was reasoned that the sodium, or potassium, or both, either in elemental or compound form, diffuse and perhaps get established in the space lattice preventing or prematurely forcing the carbides out of solution. Tools annealed in pure N_2 and heat treated in a standard manner, and tools heat treated in pure N_2, had the same type of hardness.

Pure N_2 is considered as an inert gas, and as such it appears to be when in presence of more or less excess CO; however, when pure, it diffuses into the steel, establishing itself at the space lattice forcing the carbides out.

Of course this erratic hardness is observed only on tempered tools. On tools in the as-quenched condition the Rockwell hardness coincides with file hardness which is usually 64 and 65. But the hardness of quenched high speed steel is erratic in itself and has no relation to the hardness obtained on tempering. If it were possible to quench high speed steel free of quenching stresses a hardness of 58 to 60 Rockwell C would likely be obtained. Such hardness is due to the stressing of the austenitic lattice parameter and the resulting density. However, on tempered steel the hardness is due to stresses caused by expansion of the f.c.cu. to b.c.cu. and the dispersion of submicroscopic carbides, which bring about resistance to deformation or equilibrium.

So far the subject of carbide formation and the hardness of carbides have not been discussed. This is important from the standpoint of evaluating the tungsten and the molybdenum high speed steels.

In forming a mental picture to visualize how the compounds such as carbides are being formed, one may go to an astronomer and ask him what his definition of a celestial atom is. No doubt he would say that a cosmic atom is a sun with planets revolving around it in an orbit; the sun or the positively charged nucleus with planets or negatively charged electrons revolving around it. Indeed such is an elemental atom and the difference between a cosmic and an elemental atom is only in magnitude. Can anybody imagine what would happen if between two tungsten atoms or between two tungsten suns or nuclei, around each of which 74 negatively charged electrons or planets are rotating in an orbit, if a much smaller atom such as carbon with one nucleus or sun and only 6 negatively charged electrons or planets entered?

The influence of the energy emanating from the tungsten suns upon that of carbon sun and its planets would be so tremendous that it would completely encompass the carbon atom and change its entire structure. Yet the two tungsten atoms in themselves would undergo a tremendous change partly because the influence of the carbon atom upon them and partly because of the dissipated energy upon the carbon. There would be no equilibrium in existence between the tungsten nuclei and the negatively charged electrons. The rotation of the electrons in the orbit would be slowed down because of the energy from the carbon nucleus exerted upon them, yet there would be a tendency on the part of the negatively charged electrons both tungsten and carbon to speed up their rotation in the orbit because the like charged electrons repel each other. It would be improper to say that under such conditions, where the equilibrium is absolutely destroyed, we are dealing with stresses, yet such is the case as we ordinarily understand it. Stress, whether it be cold work, quenching, alloying, compound forming is always accompanied by hardness or resistance to deformation, or disturbance in equilibrium if you please.

The disturbance in the equilibrium must be indeed great when even a property such as magnetism is lost on quenched or austenitic steels. The writer considers magnetism as an excess energy from the nucleus which is being dissipated. The dissipated energy when carbides are in solution is evidently being absorbed by them, so that such steels become nonmagnetic. The

writer in discussing Mr. H. D. Newell's paper on Properties of 18-8, in the TRANSACTIONS of American Society for Steel Treating, 1932, suggested that if 18-8 was reasonably free of carbon, such a steel which is otherwise non-magnetic would actually become magnetic regardless of what temperature it was quenched from. Dr. Krivobok made 18-8 with 0.01 per cent carbon and found it magnetic under all conditions. It goes to prove that presence of carbon is necessary to retain the gamma space lattice which even such a potent element as nickel cannot do by itself, unless it is added in larger proportions.

Having established the compound formation and its effect, namely, hardness, we can readily visualize that, depending on the type of compound, there is a corresponding hardness. WC due to its nature is harder than W_2C, because there is a greater disturbance in the equilibrium or greater stresses set up in the case of WC than in W_2C. Following the same line of reasoning, the formation of Mo_2C is accompanied by lesser degree of stressing because there are only 94 negatively charged electrons rotating in the orbit around the molybdenum nucleus giving it a density of 10.2, whereas in case of tungsten there are 184 giving it a density of 19. Therefore, we may conclude the hardness of W_2C is approximately twice that of Mo_2C. The writer on his recent visit to the Climax Molybdenum Co. learned that this company is producing molybdenum carbides (Mo_2C) on a commercial scale. On inquiring further about the hardness of this Mo_2C he was told that it is only half as hard as W_2C.

Now how are we going to reconcile ourselves to the fact that under some conditions the efficiency of the molybdenum type of high speed steel tool is equal, or better, to that of 18-4-1. An ordinary carbon steel tool if it were possible to keep it cool while cutting would be quite efficient on jobs where coefficient of friction was negligible. The writer after a considerable amount of research work established that although the heat at which a turning tool of 18-4-1 broke down was higher than that of molybdenum type yet on actual cutting, the molybdenum tool was more efficient than the 18-4-1. It was not logical yet the facts were there. Further investigation disclosed that one important factor was completely disregarded, namely, heat conductivity. Hereby lies the secret of the greater efficiency of the molybdenum type tool under some cutting conditions. The molybdenum type high speed steel has a better heat conductivity than the 18-4-1. Having better heat conductivity it is capable of dissipating the heat generated at the cutting edge to the shank, thus retaining a cooler cutting edge longer than the 18-4-1. The molybdenum type of steels without the 1.5 to 2 per cent tungsten additions were investigated; however, they were found very unsatisfactory, confirming the contention that the W_2C, even though present in small quantities, is very potent in increasing the wear resisting properties when combined with higher hardness. At the firm with which the writer is connected, to better the performance of 8-4-1-1.5 multiple cutting tools, the tools are heat treated to as high as 68-70 Rockwell C hardness. Ordinarily such a tool would be considered too brittle, yet that is no problem with us.

A great deal more may be said about the relative merits of the tungsten high speed steel as compared with the molybdenum type; however, the writer is not at liberty to discuss them in more detail.

Having established the foundation on which to judge or evaluate the merits of a given high speed steel let us consider the 4 per cent molybdenum, 5 per cent tungsten type steel which forms the subject of this discussion. In this analysis let us suppose that we have 0.80 per cent carbon and wish to resolve this in terms of carbides, we have:

5 per cent tungsten combines with 0.16 per cent carbon forming W_2C.
4 per cent molybdenum combines with 0.25 per cent carbon forming Mo_2C.
1 per cent vanadium combines with 0.20 per cent carbon forming VC

so that we have about 0.19 per cent left to form Cr_3C_2, Cr_4C and some Fe_3C. This would be an abnormal amount of chromium carbide. And indeed such appears to be the case when one examines the photomicrographs or specimens of this steel under the microscope. The writer does not consider the chromium carbides very efficient for high speed cutting. However, there is 5 per cent tungsten, which in carbide form makes up for deficiency as compared with the 8 per cent molybdenum type.

In the 8 per cent molybdenum steel about 0.50 per cent of the total carbon will combine to form Mo_2C while only 0.05 per cent will be consumed to form W_2C. In the 4-5 type we have poorer heat conductivity as due to the higher percentage of the W_2C, but this poor heat conductivity may be offset somewhat by the presence of the lower percentage of the Mo_2C, so that all in all the 4-5 type may compare favorably with the 8-1.5 type, on turning soft and ductile grades of steel. However, it is anticipated that on multiple cutting tools where the wear resisting properties are of prime importance, the efficiency will not compare favorably with that of 18-4-1 or even that of 8-4-1-1.5 type.

In considering cutting problems, one soon learns that there are too many variables to be accounted for; such as cutting oils with their volume, pressure, cooling characteristics, viscosity; type of cutting whether lathe or screw machine, broaching or gear cutting type of machine, loose spindles, bad bearings, work tool slides, poor set-ups, improper feeds and speeds; type of steel being cut, its melting and rolling practice, thermal treatment, cold working and other processing of the steel; then comes the tool with its variables that can have a profound effect upon the results obtained such as type of high speed steel, the way the tools are heat treated and ground, as well as tool and clearance angles. These are all elusive sources of trouble so that it is difficult to say whether we are observing differences in machining qualities of the metal, or the effect of the machine, or the tool or the coolants.

The writer has investigated the molybdenum type of high speed steels with copper, boron and copper-boron additions and found them inferior to the standard 8-4-1-1.5 type both as to the impact properties as well as cutting efficiency. The copper-boron type in the as-annealed state ranged in hardness, on a bar ½ inch square 6 inches long, from 18 to 32 Rockwell C. Such hardness is an evidence of an abnormal equilibrium or residual stress and if heat treated in that condition grain growth would ensue.

With regard to the decarburization, tools made of these steels when heat treated without the customary borax coating in an atmosphere control furnace did not come up to standard and as such were rejected.

The 4-5 type has not been investigated as yet by the writer. The steel

may have some merit for turning mild steels. Its value, however, for cutting higher carbon alloy steels or shaping, hobbing or milling operations is doubtful, because of its low percentage of hard carbide forming element which reduces its wear resisting possibilities.

The writer in this discussion has attempted, not to criticize the splendid work of the author in summarizing the attempts made to overcome the troublesome problem of decarburization of the molybdenum type steels, and the excellent work he himself has undertaken to bring this problem to a satisfactory conclusion, but rather to point out a way or a method to research work which would lead us to a better understanding of the fundamental principles of high speed steel. Once we have a better understanding of the basic principles involved in thermal treatments, we may then come to the solution of how to overcome decarburization.

Oral Discussion

A. H. D'ARCAMBAL:[2] Steel 282 of Allegheny Ludlum, containing 4.00 per cent molybdenum and 5.00 per cent tungsten, seems to behave quite favorably in regard to lack of decarburization. However, steel No. 283 does show decarburization, and there is so little difference in the composition of these two steels I was wondering if difficulty would not be experienced regarding proper control of the alloying elements. In other words, at times you may receive steel of the No. 282 type which would decarburize when subjected to the so-called open fire process.

R. P. DEVRIES:[3] I would like to add a few remarks apropos of what Mr. d'Arcambal has just said concerning decarburization. About 600 different analyses of steels have been melted in the range of the grade 282 in the paper under discussion. In the attempt to get a steel that was at least equal to the regular 18-4-1, the critical aspects of these steels had to be very carefully considered. Some of these aspects are so critical that the Allegheny Ludlum Steel Corp. to date have not brought out an analysis although they laid the foundation for this work in the year 1924. One of the critical aspects is decarburization.

When steels similar to grade 282, in which the tungsten is slightly higher than the molybdenum, were tested for decarburization, it was found that it was in all respects equal to the regular 18-4-1 grade of high speed steel. The test which was used to determine the amount of decarburization was to expose the steel for 3 hours at 2000 degrees Fahr. to a slightly oxidizing atmosphere and then grind off by small increments the amount of steel that has in any way been decarburized, checking the hardness at every step of grinding until stock is removed to the point where a maximum hardness and no further change of hardness is encountered.

A. G. SPENCER:[4] We have listened to the steel manufacturer, we have heard some of the reports from the tool manufacturer, Mr. McCadie has given us some information as to the uses in drill tests. I thought it might be inter-

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[3]Director of research, Allegheny Ludlum Steel Corp., Watervliet, N. Y.
[4]Metallurgist, Chevrolet Motor Co., Flint., Mich.

esting to give some of the results that we have had at the Chevrolet Motor Company in Flint, Mich.

We have been working with the steel manufacturers, for the last two years, and with some of the tool manufacturers and we are interested not only from the national economic viewpoint and the initial tool cost, but principally from the prolonged tool life and greater cutting speeds which we may expect to get.

It is not always possible to carry on extensive tests in a plant, as they interfere with production, although the plant tests are the most important and most reliable. It takes a long time to make a test in the plant; various difficulties arise; temporary conditions change the results; so that it is necessary to carry on the tests for quite a long time in order to get reliable results.

We are definitely interested in the molybdenum type of steels. So far we have only had an opportunity to test the Mo-Max type. We hope later to work with the others, including vanadium, cobalt, copper-boron, etc. We believe they have definite possibilities and while the optimum composition may not yet be reached, that as experience is gained a still better steel will be developed, and, along with other users, we are anxious to co-operate. It shows promise in our plant as a lathe tool. On some of our severest jobs—crankshafts, etc.,—we have had very good results as far as we have gone.

I might further add that it also offers possibilities, that is aside from the subject of this paper, in hot die steels. We have had promising results in that line. I thought these remarks might be of interest to the members as giving a viewpoint other than that of a steel manufacturer or a tool maker.

L. S. BERGEN:[5] Mr. Gill's comment that the paper is valuable in that it offers an opportunity for discussion is well taken. This is a subject which has not been discussed in public meetings very frequently.

After listening to this discussion on molybdenum high speed steel, I definitely feel that only confusion can exist in the mind of the user of high speed steel. High speed steel is too important to industry to allow any part of it to be in a confused state. I suppose it is perfectly natural for anything new to go through such a period. Fortunately, we have the old reliable 18-4-1 to stand behind and to use during this period.

In the discussion today, several types have been reported. At the meeting next year, there will probably be several more things mentioned. There is hope that the producers of high speed steel can get together and eliminate the confusion which exists at the present time. There seems to be a tendency to do this. I think it is in the right direction. Let us hope that before many months go by, or many years, we can have one molybdenum type of high speed steel worthy of taking its place alongside the well proven, standard 18-4-1.

Author's Reply

The author wishes to thank Mr. McCadie for his interest in Steel No. 5 and for the data in his tables giving hardness, grain size, and load required to break standard test specimens.

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[5]Metallurgist, Crucible Steel Company of America, New York.

The information contained in Mr. Armstrong's discussion is in general agreement with the author's ideas on the subject of low alloy high speed steels.

The author wishes to thank Mr. DeVries for his very complete discussion of Steel No. 5, and for the photomicrographs showing structures at various hardening and tempering temperatures.

The discussion by Mr. Fetz is very timely and of considerable interest. It indicates that foreign research confirms the author's opinion of low alloy cutting steels.

In addition to Mr. DeVries' reply to Mr. d'Arcambal regarding decarburization of Steels 282 and 283 described in Mr. DeVries' written discussion, the author would like to advise that both of these steels can be considered equal from the standpoint of decarburization under a variety of atmospheric conditions, and both steels show a degree of decarburization equal to 18-4-1.

Mr. Spencer's comments are appreciated. It is gratifying to know that high speed steel users are willing to try out new materials. It is only through such co-operation that we can determine the best combination of elements to produce a good cutting steel.

Mr. Bergen has voiced an opinion which should be seriously considered by the tool steel industry. Every effort should be made to eliminate confusion regarding high speed cutting steels.

Mr. Stotz brought out a point regarding No. 5 steel and referred to a foreign article on the subject of high speed cutting steels. In looking over this article I noticed that the author reported decarburization. All I can say is, that, with No. 5 steel as shown on the chart, we have made hundreds of tools and hardened them under all sorts of conditions, and they came out file hard. I do not know how much total decarburization might be revealed, but it appears to me that if a steel comes out of hardening file hard and with a Rockwell of 63-65 C, it is quite satisfactory.

Mr. Stefanides is to be complimented on the very complete theoretical discussion of the role played by the various carbide-forming elements in high speed cutting steels. In his discussion on page 332 a prediction is made regarding No. 5 steel with an analysis of 5 per cent tungsten, 4 per cent molybdenum, and 1 per cent vanadium. I would like to point out that a better analysis representative of this grade would be 5 per cent tungsten, 4 per cent molybdenum, and 1.50 per cent vanadium. This would reduce the amount of carbon left to form chromium carbides, and, following Mr. Stefanides' reasoning, this change would improve performance. Since introducing No. 5 steel, we find that it not only performs satisfactorily on soft materials but shows equally good performance on hard steels and cast materials. It has also been used to advantage on applications where wear resisting properties are of prime importance. As soon as more of No. 5 steel has been used on a variety of cutting operations we will be in a better position to make a worthwhile appraisal. Up to date the performance has been very encouraging.

In addition to the oral reply given to Mr. Gill's discussion, I would like to say that the two additional reasons given by Mr. Gill for prompting the development work in molybdenum high speed steels appear to be well covered in my second reason, namely, to produce a better cutting steel with molybdenum as the predominating alloying element. Mr. Gill requests information on the

number of samples used in determining the Izod impact values, and if he will refer to Table I it states that the values are the average of four determinations, and the samples were unnotched. Variation in results was within 25 per cent. As stated in my paper, the Izod test values were secondary in importance to the actual tool performance when considering toughness. It is unnecessary to discuss decarburization any more than has been done in the paper, since as Mr. Gill himself states, "The discussion is merely academic as both steels decarburize to such an extent that their surface must be protected, and when the surface of either is protected there is positively no difference in their tendency to decarburize." In this statement Mr. Gill is referring to the molybdenum-tungsten and molybdenum-vanadium types of steel.

I believe the points brought out by Mr. Gill are of sufficient importance to warrant some consideration before answering in detail. I did not have a copy of his discussion to look over before the meeting. However, there are one or two things which we might clear up. Mr. Gill compares the molybdenum steels with 18-4-1 in part of his paper, and I did not attempt to make any such comparison in mine. The reference with regard to the work at Watertown Arsenal is one point where we differ. I mentioned in the paper that the use of molybdenum-vanadium cutting steels anticipated the *present* molybdenum-tungsten type, and by that I meant the Mo-Max type shown in the first line of the chart. I did not refer to any of the other tungsten compositions which are not used now.

Several of the discussers mentioned the Izod test. I do not take any issue on this test, and I believe that Mr. Gill and the rest of us are in agreement as to just how much this type of test means. I merely included it to show that the steel does absorb some energy before it breaks. What we are interested in is whether or not it makes a tool, and when we endeavored to appraise the toughness we thought the best thing to do was to look over hundreds of tools to see whether they chipped or broke, and we found that they did not. I stated in the paper that the molybdenum-vanadium materials were as good as any of the other molybdenum steels as to this property.

It appears that Mr. Gill and I are at odds regarding decarburization. The difference is not great, and I believe we should hear from some of the users. I know a number of users have tried out both types—so let them be the judges. Both steels decarburize quite heavily, but if hardened in a salt bath or if a borax coating is used, neither of them decarburizes.

ABSOLUTE HARDNESS

By E. G. Mahin and G. J. Foss, Jr.

Abstract

In the field of hardness testing many studies have been devoted to the effort to distinguish between the intrinsic resistance of a metal to permanent deformation and the added resistance due to strain hardening, occurring after permanent deformation has begun. Both of these properties are included in the conventional hardness tests, with any of the currently used testing machines. The experimental determination of the first named property, which has been termed "absolute hardness," is difficult. While several attempts have been made to accomplish such a determination, more attention has been paid to theoretical deductions.

In the present paper these experimental determinations and some theoretical deductions which have been made from conventional hardness tests are discussed. A method is reported, which is believed to be new, for the direct determination of absolute hardness. While this method is not at present applicable to routine testing it does appear to be reasonably accurate and free from many of the errors incident to other reported methods.

THE voluminous literature dealing with the subject of hardness is sufficient indication of the importance of this property and of the interest with which it is regarded. This interest is most manifest in connection with metallurgical questions because, among materials in general, metals are outstanding in their usefulness in applications based upon strength characteristics.

In addition to the many papers that have appeared, special mention should be made of O'Neill's thorough treatment and summary in his book upon the subject of hardness (1)[1] and of Williams' series of papers (2), now being published. It is not proposed to undertake an extended discussion of the fundamental causes of resistance to penetration, scratching, abrasion or wear, or of the princi-

[1]Numerals enclosed in parentheses, in the text, indicate citations in the reference list, at the end of the paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, E. G. Mahin is professor of metallurgy and head of the department of metallurgy, University of Notre Dame, and G. J. Foss, Jr., is graduate assistant in metallurgy, University of Notre Dame, Notre Dame, Indiana. Manuscript received June 22, 1938.

ples involved in the many methods for measurement of "hardness," except as they may be involved in the discussion of what has been termed "absolute hardness." These matters have been extensively treated in special papers and in publications to which general reference was made, above. It is desired to emphasize, however, as many others have done, the difficulties involved in the attempt to arrive at a satisfactory and acceptable definition of the term "hardness" itself, and the wide discrepancies in such definitions and testing methods. Almost anyone is inclined to feel that he understands the general meaning of the term. Nearly everyone experiences difficulty in expressing this meaning in a manner that will be practically useful and, at the same time, free from theoretical objections.

Suggested definitions have ranged all the way from "—resistance to permanent deformation" (Jeffries and Archer) (3) and "—the intensity of the maximum pressure—which just produces yielding—" (Honda) (4) to the expression of hardness numbers obtained by use of any of the standard commercial testing machines. The conceptions covered by the first two, above quoted, may be regarded as fundamental in nature and they obviously lay emphasis upon the inherent capacity of a material for resisting applied stresses without thereby suffering any fundamental alteration in internal structure, while the expressions of the second class refer to practical determinations of *ultimate* resistance to *continued alteration* in form.

Hardness as evidenced by resistance to scratching, abrasion or wear will not be discussed in this paper. Certain elements of empiricism involved in such tests would appear to preclude the possibility that they should ever attain the status of anything more than practical tests, of practical value but incapable of very scientific interpretation. It is sufficient, for the present analysis, to confine the discussion to indentation (penetration) hardness and to its measurement.

It is generally recognized that all of the conventional hardness tests, as applied to metals, measure finally the resistance of a strain-hardened material and that they provide no indication whatever as to the resistance capacity of the metal as it was before the hardness test was begun, as covered by the conceptions of Honda, Jeffries and Archer, and others. This distinction is not, by any means, a purely academic one. It may be likened, in a manner, to the distinction between proportional limit (or yield point) and ultimate strength, as determined in a tensile test. If the designing engineer could know

only one of these values, he would consider the yield point as of far greater importance than the ultimate strength, since a metal part ceases to be useful in a permanent sense, in a structural part or a machine, as soon as it has suffered permanent deformation. If the engineer could be provided with no information concerning the behavior of a metal in the early part of the test he would experience considerable difficulty in the designing of structural parts, as based merely upon a knowledge of the ultimate strength of strain-hardened metal. This would be true even if ultimate strength were commonly reported upon the correct basis of cross sectional area at the "neck," instead of upon the present conventional basis of the original cross sectional area of the unstrained material. For here, as in hardness tests, severe cold working has been accomplished and the final measurement has been made upon strain-hardened metal. Were a convenient test available in the field of hardness characteristics, surely the engineer would be more interested in knowing the maximum unit stress which could be supported by the material without permanent deformation taking place, than in the stress which would be supported after permanent deformation, with its resulting strain hardening, has occurred.

In hardness testing the situation is even worse than in tensile or compressive testing. In the tensile test, for example, one may at least assume that at the point at which failure finally occurs the strain hardening effect has a certain degree of uniformity of distribution over the entire cross section. No such situation obtains in a hardness test, and two or three of the more widely used tests may be cited as illustrating this statement.

From the standpoint of mathematical expression the Brinell test, while not applicable to all fabricated parts, approaches an ideal test as closely as any, especially if the Brinell numbers are calculated by the modification suggested by Meyer (5). Using this modification, which substitutes the area of the projection of the impression for the surface area of this impression, the Brinell-Meyer number becomes the maximum unit stress supported by the material under test. The Brinell ball being a sphere, the effect of deformation upon the properties of the metal is at least uniform around the entire azimuth in any horizontal section including deformed metal. But the case is different when we consider, instead, a vertical section including the diameter of the impression. Neglecting, for the moment, the excessive plastic flow which occurs near the surface of the test speci-

men and immediately surrounding the impression, incident to the "piling up" effect, the cold work and strain hardening are most severe in the immediate vicinity of the impression, diminishing as the distance from the penetrator increases and finally dropping to zero. The straining is not even uniform at any given distance from the penetrator, usually being greatest at the surface of the test piece.

The final measurement of the Brinell impression and calculation of Brinell hardness are based upon neither the hardness before straining occurred nor that which represents the maximum straining effect, but rather upon some sort of vague and variable mean of these properties. When to this uncertainty is added the continuous variation of effect with increasing penetration, due to continuously changing mathematical relations between deforming metal and the penetrating spherical ball, it would appear that this test, justly favored from the commercial or practical standpoint, is still far from being an ideal test, even if the desirable Meyer modification in expression were to be universally adopted—as we believe, with Hoyt (6), should be done.

The Vickers test is one which has gained much favor. This apparently is due to four points of superiority to the Brinell test: 1. The mathematical relation of the surface of the pryamid indentor to the axis of stress has been fixed by at least an approach to scientific correctness and it does not change with increasing depth of penetration, as is the case with a spherical indentor. 2. The method is more flexible in application, due to selective variation of load over a wide range. This makes the test applicable to materials of widely varying hardness and to shallow cases, either harder or softer than the mass beneath. 3. The surface of the material is not seriously marred and a relatively small area is required for the test. 4. The use of a diamond penetrator instead of the hardened steel of the usual Brinell ball. (The last-mentioned point of superiority has been rendered less important by the introduction of harder balls, of cemented carbides, but it is still to be considered.)

Possessing these points of superiority to the Brinell test, it seems unfortunate that the selected design of the Vickers penetrator should have been that of a pyramid, rather than of a cone. Plastic flow, with resulting strain hardening, is not uniform in any horizontal section about the pyramid, as it is about a spherical or conical penetrator. And, whether or not the theoretically derived solid angle of 136 degrees employed for the Vickers pyramid is best, the Rock-

well cone does avoid one of the irregularities of plastic deformation, as above mentioned. It may be remarked also that the theoretical derivation of the Vickers angle rests upon a premise that is highly empirical and that the theory becomes less impressive when this is considered.

Without undertaking any further discussion of other hardness testing methods we may return to the statement that all fail to determine the hardness of undeformed metal, expressed in any terms. This is the fundamental reason for the impossibility of deriving any formula, based upon the mathematics of the tests, by means of which interconversion of the various hardness numbers may be accomplished. All of the theoretically derived formulas must include certain empirical corrections for variable strain hardening effects and all fail to cover hardness numbers obtained by testing metals and alloys of different character. All tests cause strain hardening and this is different in character and distribution as we pass from one testing machine to another. It varies also among the different metals and alloys, according to variation in what has been called "strain hardening capacity" of the metal itself. Obviously, all of the many proposed conversion tables, obtained by experimental comparisons, are unsatisfactory for the same reasons.

These observations should not be construed as minimizing the importance or the usefulness of hardness tests as they are now conventionally made. The situation is not essentially different here from that obtaining in other fields of testing. One does not regard the absence of fundamentally scientific testing methods as a valid reason for rejecting more empirical methods, which may still give information of great value to those who deal with engineering problems. If such methods will yield results which may be correlated with service fulfillments, a great deal is accomplished by making the tests. One would not, for example, reject the Charpy, the Izod or other standardized impact tests, merely because of the difficulties involved in defining "impact strength" or in devising a scientific method for measuring it.

The various conventional hardness tests, as they are today employed and utilized, are of great value to the metallurgist and to the designing engineer and they will, no doubt, continue to be widely used, with such refinements as may be developed by continued research. This fact, however, does not deter us from seeking further light upon the ever-present query as to the initial capacity of the

metal for resisting deforming stresses, before it has been altered by strain hardening tests. Following the lead of Auerbach (7) this capacity will be designated as "absolute hardness," which we should like to have defined as *the maximum unit stress which a material will support without permanent indentation.*

The use of the limiting term "indentation" in this proposed definition is considered as important. While it is recognized that the quality of resistance to indentation is based upon the same properties of the metal as give it resistance also to deformation through the application of stresses applied in any other manner (at least by slow loading), we do not at present see that anything is to be gained by introducing the many complicating factors that are involved in scratch, abrasion, or wear tests. Much less do we see how impact hardness tests can be included, since all of such tests include all of the uncertainties and irregularities of conventional static hardness tests, together with an almost total lack of understanding of why a metal behaves, in a shock test, so differently from its behavior under static loading.

Irrespective of modifications or refinements that may be made in the various conventional hardness tests, as a result of further study, it would be best to call all of these "hardness numbers," as distinguished from "absolute hardness," and this terminology will be followed in the present paper. As Hoyt (6) and many others have suggested, it would be preferable to abandon the present method of calculating Brinell numbers in favor of Meyer's modification, which is at least mathematically correct. As already mentioned, Meyer called attention to the fact that, in order that hardness numbers may express unit stress and that they may be mathematically free from variation incident to the changing depth of penetration of a spherical indentor, the applied load should be divided by $\frac{\pi d^2}{4}$ (the area of the projection of the impression) instead of by $\frac{\pi D}{2}(D - \sqrt{D^2 - d^2})$, the spherical area of the indentation, where D = diameter of the penetrating sphere and d = diameter of the circular projection of the impression. If this change should be adopted the new values would be reported as "Meyer hardness numbers," and this term will be used in the succeeding pages of this paper.

By the Meyer equation, $H = \frac{4P}{\pi d^2}$, where P = load, in kilograms, d = diameter of the projected impression, in millimeters, and H = Meyer hardness number (unit stress, in kilograms per square millimeter). The Meyer hardness number is then an inverse function of the square of the diameter of the impression and the relationship of load and impression diameter is expressed by $P = ad^n$. Hoyt (6) called attention to the fact that if d, in this equation, is 1 mm., $P = a$. The constant a then indicates the resistance of the metal to initial penetration and the value of the exponent n is an indication of the effect due to strain hardening occurring during the progress of the test. Assuming the validity of the Meyer equation, Hoyt's conclusion is mathematically correct. It is based upon the arbitrary assumption, however, that strain hardening begins only after the diameter of the impression passes 1 mm., a condition which naturally is not realized in practice. Considering the ball penetrator as a perfect sphere and the tested surface as a perfect plane, the initial area of contact approaches zero and any finite pressure gives a value for unit stress approaching infinity. As penetration proceeds, yield (elastic, inelastic, or both) occurs and the unit stress, at constant loading, decreases. It is obvious that if the recovered impression has a diameter of 1 mm., or any other measurable quantity, strain hardening has resulted.

Another error in this method for deriving values for a and n rests upon the selection of 1 square millimeter as the unit of cross section. If any larger or smaller unit were used, a and n would not only have different numerical values—they would also have different relative significance.

The assumed significance of a and n in Meyer's equation is therefore only an approximation, although useful in lack of anything better. In the entirely hypothetical case of a metal which would experience no strain hardening, n would have the value 2.0. This case is approximated by lead, which recrystallizes at ordinary temperatures after straining, or by other metals tested at temperatures within zones of recrystallization. The exponent $n - 2$ could then be taken as a measure of strain hardening capacity, since n is always greater than 2. On account of the variable character of straining resulting from a hardness test, already discussed at some length, an element of empiricism must always remain with this method of interpretation of the significance of n. It must be realized also that the strain hardening effect in the zone affected by the penetration can

never even approach the maximum strain hardening capacity of the metal.

The Direct Measurement of Absolute Hardness

Although Meyer's equation, $P = ad^n$, provides a certain amount of information concerning the relative parts played by original hardness and strain hardening additions, in a conventional hardness test, the interpretation of the numerical values of a and n is still somewhat obscure and a method for the direct experimental determination of absolute hardness is desirable.

Harris (8) performed such a determination. A conventional Brinell hardness determination was first made. The specimen was then annealed in an atmosphere of hydrogen in order to remove the strain hardening effect. The Brinell ball was replaced in the first impression and the load was again applied, the ball penetrating farther into the now unstrained metal and thus producing additional strain hardening. This process of applying load, followed by annealing, was repeated until there was no measurable additional penetration and the final diameter of the impression was used in the calculation of absolute hardness. Ten annealings were required in order to reach the final maximum diameter of the impression.

This method is necessarily tedious, as it appears that any experimental method for such a determination would be. But attention must be called to other objections. In the first place such a method of repeated testing and annealing can only approach the ultimate volume of impression. Also it should be noticed, in this connection, that straining followed by annealing produces grain refinement, this increasing the hardness of the refined zone. The final measurement of the impression, therefore, is calculated to the absolute hardness of a material which, at least in the vicinity of the impression, is harder than the original untested material. This hardness difference may not be large but it introduces an uncertainty, which is further complicated by possible grain size or structural changes in the unstrained body of metal.

It may be further pointed out that Harris' method for determining absolute hardness by "strainless indentation" is inapplicable to any alloy system which is not already in a condition of phase equilibrium at the beginning of the test. It could not be applied, for

example, to an age-hardening alloy which has not been thoroughly annealed before testing, or to any heat treated steel.

Loritsch (9) undertook to determine the effect of grain refinement occurring during the progress of the test by the method of Harris, using a variety of ferrous and nonferrous alloys. After each piece had been given its first Brinell test and annealed, he ground the tested surface just to the bottom of the Brinell impression. Vickers 1-millimeter ball tests were then made at the center of the zone affected by the Brinell deformation and subsequent annealing, as well as on the body of the piece. Variable increases in hardness were found, amounting to as much as 10 per cent, based upon the original ball hardness numbers.

Previous to the work of Harris, Thomas (10) had undertaken a somewhat similar investigation upon "mild steels," but his annealing processes apparently were performed in air, as he mentions the removal of scale after each annealing. Such a procedure necessarily involved surface decarburization, as well as grain size changes incident to the method of Harris. His conclusions, therefore, would appear to be of questionable value. Both Thomas and Harris obtained values for absolute hardness which were very much lower than either Brinell or Meyer values.

Franke (11) attempted to determine absolute hardness by determining scleroscope or pendulum hardness at the bottom of a Brinell impression, calculating initial (absolute) hardness from the formula, $H_i = H \times P_o/P$, in which H = Brinell number, H_i = initial Brinell number, P_o = pendulum or scleroscope hardness of the original material, and P = hardness at the bottom of the impression. The errors incident to this procedure are numerous. The determination of P_o involves strain hardening, as does any other conventional method for the determination of hardness. The value of P cannot be considered as indicating a mean effect and the final determination involves still further hardening. Franke's results, therefore, while interesting, must be regarded as only qualitative in nature.

Sauveur and Burns (12) worked upon lines somewhat similar to those of Franke and similar comment is in order.

Baker and Russell (13) showed that if a metal be increasingly cold-worked, n in Meyer's equation approaches the numerical value of 2. By a more or less qualitative extrapolation the conclusion was reached that, if a metal should be cold-worked to the ultimate possible degree before testing, Meyer's equation would become $P = ad^2$,

indicating that the theoretical maximum hardness of the cold-worked metal had been reached. Although this does roughly appear to confirm the correctness of the Meyer equation, it gives no indication whatever as to the absolute hardness of the original unworked metal.

McAdam (14) obtained similar results upon progressively cold-worked nickel. As the degree of cold working increased, n decreased, reaching a value of 2.03 for the most highly worked metal. This would indicate a close approach to the ultimate strain hardening capacity of the nickel.

All of these researches point toward the essential validity of the Meyer equation, in which a is a factor whose value depends upon the absolute hardness and $n - 2$ is an index of work hardening capacity. If the Meyer equation could be confirmed as a correct quantitative statement of the relations existing among the values represented by it, this equation would become a useful tool for deducing important properties of metals and alloys. That such deductions are approximate only is a conclusion that should be obvious from the evidences of empiricism, as recounted in the preceding discussion. That they are, in many cases, far from being quantitatively correct should be concluded from the results of the experimental work to be described.

Experimental

In order to avoid, in the determination of absolute hardness, all possible errors incident to grain size or other structural changes and to strain hardening effects in test specimens, the procedure of forming impressions by *removing*—instead of by *displacing*—metal corresponding to the volume of the test depression was adopted. The Brinell method of applying the test was used as an experimental medium but Meyer's modification was used for all calculations of hardness numbers. (Brinell hardness numbers are given in Table II, for purposes of comparison.)

Two forms of tools were fabricated for use in these tests by well-known manufacturers. Several two-fluted, centerless drills of high speed steel, having a spherical cutting front with a radius of 5 millimeters, were made. A drill was fixed in the tail stock of a lathe, the test specimen being rotated in a four-jaw chuck placed in the head stock, and spherical depressions of the form of the Brinell impression were made in the test specimen by this means.

Grinding tools having the same form and radius as the drills

were made from alundum of two different grits. It was the original intention to use these grinding tools for forming depressions in materials too hard to be drilled but this was found to be impracticable, chiefly because of the impossibility of producing a grinding effect at the axis of the tool, by simple rotation. The grinding tools were finally used only for finishing the formation of a depression of correct dimensions, by hand manipulation. Certain changes in the design and manipulation of these tools are contemplated and it is expected that determinations of absolute hardness of heat treated steels and of other hard materials will later be made possible.

The usual simple Brinell measuring microscope was not used for measuring the diameters of any of the depressions. This form of measuring device is subject to so many errors, of parallax and approximations of readings, that it is considered as inapplicable to experiments of any considerable degree of precision. Instead, a measuring microscope, bearing cross hairs and having an outside scale, was employed. This microscope is moved horizontally by a screw of fine pitch, an outside micrometer scale making readings to 0.001 millimeter easily possible. The reading precision was thus considerably greater than was justified by the precision possible in the test itself.

In the performance of a determination of absolute hardness the procedure was as follows: The test piece was first prepared from a bar of rectangular cross section, of ample dimensions to eliminate any possible errors due to small section. Surface grinding was employed to bring this specimen to a smoothness which would make possible sharp observations of the boundaries of the circular projections of impressions.

An orthodox Brinell test was then applied and, after measuring the diameter of the impression, both Brinell and Meyer hardness numbers were recorded. The test specimen was placed in the lathe chuck and a series of depressions, of various depths and diameters, were drilled in the prepared surface. After some experience with a given material it was found not difficult to include the probable required depression dimensions for the absolute hardness test within a comparatively narrow range of experimental dimensions. The Brinell ball was then carefully centered in each of the drilled depressions and the load used in the Brinell test was again applied.

In the usual course of events, some of these depressions were enlarged by the reapplication of load while others were not. These

observations served as a guide to the forming of other drilled depressions, covering a still narrower range of diameters. The grinding tools were used, at the last, for forming to the highest possible degree of precision. These tools were employed with hand operation, as was stated above, a combination of twirling with gyratory motion being used.

When a depression had finally been produced, the dimensions of which were just sufficient to support the Brinell load without further deformation, the measured diameter was converted into absolute hardness by use of the modified Meyer formula, $A = \frac{4P}{\pi d^2}$.

Possible errors which might be supposed to affect the accuracy of this experimental method for the direct determination of absolute hardness rest chiefly in the matter of precision in the form of tools for forming the depressions and in the formation of a layer of cold-worked metal over the surface of the depression. As to the first, no doubt it will be possible to have somewhat better tools constructed for future determinations, as the importance of further refinement may develop. But, so far as could be determined by a trial seating of the Brinell ball in a formed depression, the precision as to form and radius was satisfactory for the present purpose.

The depth of any surface layers of cold-worked metal formed by mechanical actions involved in drilling and grinding was not believed to be sufficient to affect the results appreciably, especially since all forming operations were carried out slowly with sharp drills and clean grinding surfaces.

Brinell impressions for Meyer hardness numbers were determined at two or more loads on each specimen to determine the most suitable load for an impression whose diameter would be within the limits of 2.5 and 5.0 mm. according to standard practice, and to obtain two or more equations of the form $P_1 = ad^n_1$ and $P_2 = ad^n_2$ which, in logarithmic form, could be solved for values of a and n. Comparison of these derived values with similar values obtained from the direct determination will be found in Table III.

Experimental Materials

The various metals and alloys, with heat treatments, are listed in Table I. These materials were selected partly from the standpoint

of availability and, in the case of age-hardenable alloys, partly in order to gain some light, if possible, upon the question as to whether straining of such alloys causes precipitation hardening, when tested in the quenched condition.

Table I
Nature and Treatment of Alloys Used for Hardness Tests

Spec. No.	Description and Treatment
1	Beryllium-copper alloy, Be = about 2 per cent
	(a) Annealed at 800 degrees Cent. (1470 degrees Fahr.), furnace cooled
	(b) Quenched in water from 800 degrees Cent. (1470 degrees Fahr.)
	(c) Same as (b), then aged at room temperature for 720 hours
	(d) Same as (b), then aged at 275 degrees Cent. (530 degrees Fahr.) for 18 hours
	(e) Same as (b), then aged at 275 degrees Cent. for 5½ hours
2	Tool steel, C = 1.0 per cent, annealed at 900 degrees Cent. (1650 degrees Fahr.)
3	Extruded Dowmetal F bars, as received
4	Extruded Dowmetal J bars, as received
5	Magnesium metal bars
6	Beta brass, as received
7	Copper
	(a) Cold worked, then heated at 800 degrees Cent. (1470 degrees Fahr.) for 24 hours
	(b) Hot worked
8	Armco ingot iron
	(a) Hot worked, then heated at 950 degrees Cent. (1740 degrees Fahr.) for 168 hours
	(b) Drastically hot worked from 950 degrees Cent.
9	Alcoa aluminum alloy 17s
	(a) Annealed at 510 degrees Cent. (950 degrees Fahr.), quenched in water
	(b) Same as (a), then aged at 155 degrees Cent. (310 degrees Fahr.) for 18 hours
	(c) Same as (a), then aged at room temperature for 720 hours
10	Alcoa aluminum alloy 51s
	(a) Annealed at 505 degrees Cent. (940 degrees Fahr.), quenched in water
	(b) Same as (a), then aged at 155 degrees Cent. (310 degrees Fahr.) for 18 hours
	(c) Same as (a), then aged at room temperature for 720 hours

In the interest of brevity, the results obtained by the use of two or more Brinell loads are not reported in Table II. Only the one load which was found, in each case, to give an impression of size suitable for the calculation of the Meyer hardness number is included, the others being used only for the calculations of Meyer's a and n.

In all cases the numerical expression for absolute hardness was found to be much lower than for the Meyer hardness, as might be expected. The ratio $\frac{M}{A}$ was greater than 2.0 in most cases and nearly 2.0 in the few exceptions—Armco iron and one aged aluminum alloy. This is, of course, in harmony with existing conceptions.

The greatest interest, in this connection, attaches to the comparison of a and n values as indices of original hardness and of work

Table II
Experimental Data and Calculated Hardness Values

Spec. No.	Load, kilograms	Brinell Diam., mm.	Absolute Diam., mm.	Brinell number	Meyer number	Absolute hardness	Meyer hardness number / absolute hardness
1a	2000	4.12	6.14	143.1	149.8	67.5	2.22
		4.99	6.07	144.7	152.2	69.1	2.20
		4.05	6.06	148.0	155.0	69.3	2.24
1b	2000	4.56	6.86	116.8	122.4	54.1	2.26
		4.50	6.19	119.9	126.6	61.1	2.07
		4.55	6.75	116.7	125.3	55.9	2.24
		4.58	6.98	115.7	124.5	52.3	2.38
		4.54	6.53	117.8	125.6	59.7	2.10
1c	2000	4.50	6.75	121.0	128.9	55.5	2.33
		4.58	6.51	113.6	120.5	60.0	2.01
		4.61	6.95	112.7	119.8	52.7	2.27
		4.63	7.01	111.6	118.8	51.8	2.29
		4.59	6.88	113.6	120.9	53.9	2.24
1d	3000	3.42	5.05	318.5	328.5	149.2	2.20
		3.38	5.04	323.5	334.5	150.8	2.22
		3.43	5.04	318.0	325.5	150.0	2.17
1e	3000	3.42	4.98	318.0	326.0	153.9	2.12
		3.42	4.97	318.0	326.0	154.6	2.11
		3.33	4.94	338.0	344.0	156.4	2.20
		3.24	4.92	356.8	363.1	157.9	2.30
		3.20	4.90	364.0	371.0	159.0	2.33
		3.23	4.92	353.6	367.0	157.6	2.33
		3.22	4.92	357.0	369.0	158.0	2.34
2	3000	4.65	7.04	167.5	176.8	75.7	2.33
3	500	3.53	5.63	49.7	51.2	20.1	2.55
4	1000	4.67	7.20	54.9	58.5	20.8	2.39
		4.68	7.24	54.4	58.1	24.3	2.40
5	1000	4.98	7.60	47.8	51.0	22.0	2.32
		4.96	7.59	48.2	51.9	22.1	2.34
6	2000	4.59	6.55	113.7	120.9	58.9	2.04
		4.57	6.52	114.7	121.8	59.9	2.03
7a	500	3.87	6.34	41.0	42.6	15.9	2.69
7b	500	3.76	5.90	43.3	45.1	18.3	2.47
8a	1000	3.94	5.22	78.7	82.0	46.0	1.73
8b	1000	3.86	5.25	83.0	86.0	46.1	1.87
9a	500	2.64	3.83	89.7	91.5	43.4	2.11
		2.78	4.04	81.3	82.7	39.6	2.09
		2.77	4.02	81.6	83.1	40.0	2.08
		2.77	4.04	81.6	83.1	39.7	2.10
	1000	3.93	5.44	81.0	82.5	43.1	1.92
9b	500	2.40	3.52	109.0	111.6	51.3	2.18
		2.42	3.52	107.2	108.2	51.5	2.10
		2.48	3.50	102.6	103.9	51.9	2.00
		2.44	3.50	106.1	106.9	51.9	2.06
		2.49	3.51	101.1	103.2	51.7	2.00
9c	500	2.50	3.74	99.5	101.8	45.6	2.23
		2.47	3.60	102.7	104.8	49.0	2.14
		2.48	3.67	102.1	103.8	47.3	2.19
10a	500	3.96	5.82	37.4	40.6	18.8	2.16
		3.98	5.83	38.6	40.2	18.7	2.15
		4.04	5.83	37.5	39.7	18.7	2.13
		4.04	5.82	37.5	39.7	18.8	2.11
10b	500	2.61	3.65	92.2	93.5	47.9	1.96
		2.63	3.69	90.9	92.0	46.8	1.97
		2.69	3.68	86.1	88.3	47.0	1.88
		2.69	3.68	86.1	88.3	47.0	1.88
		2.67	3.68	88.4	88.3	47.1	1.87
10c	500	3.35	4.92	55.0	56.8	26.3	2.16
		3.19	4.87	61.2	62.4	26.9	2.32
		3.20	4.75	60.1	62.4	28.2	2.21
		3.18	4.66	61.2	63.2	29.3	2.15

hardening capacity, respectively, first as determined from Brinell impressions under two or more loads, and second as calculated from direct determinations of absolute hardness. These comparisons are given in Table III.

Table III
Comparison of a and n Values of Meyer's Equation, $P = ad^n$, as Obtained by Different Methods

Spec. No.	From Meyer Numbers at Different Loads		From Absolute Hardness Determinations	
	a	n	a	n
1a	80.8	2.27	53.9	2.57
1b	57.5	2.32	44.8	2.52
1c	57.9	2.39	43.0	2.54
1d	156.5	2.24	117.8	2.64
1e	166.0	2.22	123.2	2.68
2	69.2	2.43	59.5	2.74
3	21.6	2.49	15.8	2.74
4	16.5	2.66	19.1	2.56
5	26.2	2.29	17.3	2.53
6	58.0	2.34	47.0	2.47
7a	14.0	2.66	12.5	2.73
7b	15.8	2.61	14.4	2.68
8a	43.0	2.35	36.1	2.40
8b	52.5	2.18	36.2	2.46
9a	43.2	2.42	34.0	2.47
9b	52.9	2.22	40.6	2.81
9c	50.9	2.28	37.2	2.86
10a	17.5	2.42	14.7	2.55
10b	54.4	2.20	37.0	2.67
10c	33.3	2.27	21.8	2.68

Note: The values listed in the last two columns of this table have been calculated from averages shown in Table II, for each specimen, and not from individual experiments.

For the derivation of a and n values by the first method, the hardness determination is carried out with two different loadings, P_1 and P_2, giving impression diameters d_1 and d_2. Since $P_1 = ad^n_1$ and $P_2 = ad^n_2$, then $P_1d^n_2, = P_2d^n_1$, and $n = \dfrac{\log P_1 - \log P_2}{\log d_1 - \log d_2}$. The substitution of experimental values for pressures and diameters enables one to calculate n. This value may then be substituted in the equation $P = ad^n$ and the value for a calculated.

The calculation of a and n from direct determinations of absolute hardness is even more simple. If M = Meyer hardness number and A = absolute hardness, $M = \dfrac{4P_M}{\pi d^2_M}$ and $A = \dfrac{4P_A}{\pi d^2_A}$. Pressures and diameters may have different values in these expressions but it is convenient to consider the diameters of the Meyer and absolute impressions the same, so that $d_M = d_A = d$. Substituting the

appropriate values for P: For the Meyer hardness number, $P_M = ad^n$ and $M = \frac{4ad^{n-2}}{\pi}$. For absolute hardness, $P_A = ad^2$ and $A = \frac{4ad^2}{\pi d^2} = \frac{4a}{\pi}$. For the ratio of Meyer hardness to absolute hardness, $\frac{M}{A} = d^{n-2}$. (In this equation d is the diameter of the Meyer impression.)

The equation $\frac{M}{A} = d^{n-2}$ may be written logarithmically as $\log \frac{M}{A} = (n-2) \log d = n \log d - 2 \log d$. From this, $n = \frac{\log M/A}{\log d} + 2$. If experimentally determined values for M, A and d are substituted in this equation the solution for n becomes a simple one.

The value for the Meyer a is obtained from the equation $A = \frac{4a}{\pi}$. From this, $a = \frac{\pi A}{4}$. Since A has been determined directly, a is easily calculated.

These calculated values for a and n appear in the last two columns of Table III.

Summary and Conclusions

1. An experimental method has been devised for the direct determination of absolute hardness. This method is based upon the *removal* of metal instead of upon its *displacement*, and strain hardening effects are thus entirely avoided.

2. From the results of such a direct determination the calculation of values for a and n of Meyer's equation may be made without resorting to the use of Brinell determinations under different loadings.

3. In all of the experimental determinations upon alloys listed in this paper the a value was found to be lower, and the n value higher, than as calculated from two Brinell tests. Irregularities in strain hardening effects as the load is increased are considered to be responsible for much of this difference. For this reason the direct determination is thought to possess greater dependability. From an inspection of the data of Tables II and III it will be concluded that the interdependent values of absolute hardness and the constant a

are lower than they have usually been considered to be, for all of the alloys involved in this investigation. It seems probable that this would be true also for most other alloys.

4. Even as derived from determinations of Meyer hardness numbers and of absolute hardness, n of Meyer's equation cannot represent the ultimate strain hardening capacity of a metal. The only meaning that may safely be assigned to it is that of an index of strain hardening taking place during the application of the conventional Brinell test.

5. So far as would be indicated by the few cases involving grain size differences, as reported in this paper, variation of grain size within ordinary limits has little effect upon work hardenability. Specimens of copper of coarse and fine grain (7a and 7b) show a slight advantage in n for coarse grains. On the other hand, similar specimens of Armco iron (8a and 8b) indicate the opposite effect. The difference is not large, in either case, but the results obtained upon these four specimens are not regarded as conclusive.

6. The tests upon age-hardenable alloys of beryllium-copper or duralumin types give little ground for supposing that hardening by dispersion precipitation occurs to any important degree, when quenched solid solutions are strained. The value of n for the quenched beryllium-copper alloy (1b) is not higher than for the same alloy in other conditions, either annealed or quenched and aged. The same observation may be made in the case of aluminum-copper alloys. In fact, so far as any difference appearing in the tabulated results would indicate, the quenched alloys show a slight inferiority in this respect.

These cases are not at all analogous to that of retained austenite in steels, converted into martensite by straining. In austenite at ordinary temperatures, iron is in the gamma state and highly metastable. It might be expected that the phase change of gamma to alpha iron would be promoted by straining and that the alloy would become much harder on account of the formation of extremely fine-grained martensite, even if no precipitation of cementite at all should take place.

Straining of the metastable (supersaturated) alpha beryllium-copper solution might cause a tendency toward precipitation of the beta solution. But it is not easy to see how migration of beryllium could take place at ordinary temperatures to the extent necessary for the formation of beta crystals of critical dimensions. A similar

observation should apply to the quenched aluminum-copper solid solution, and possible precipitation of the compound Al_2Cu.

7. Certain plans have been made for application of the direct method to the determination of absolute hardness of very hard alloys. If these are perfected it may be possible to obtain further light upon the properties of metastable systems and of heat treated steels.

8. It is hoped that a method and a form of apparatus may be devised for accomplishing more rapid determinations of absolute hardness. No prediction is made as to whether such determinations may become practical testing methods. In any event they should be useful for investigations in the field of fundamental properties of metals and alloys.

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DISCUSSION

Written Discussion: By J. J. Kanter, research metallurgist, Crane Co., Chicago.

The measurements of the resistance of unworked metal to ball indentation which the authors have so ingeniously and painstakingly accomplished are a welcome contribution to our information on indentation resistance. The value of their investigations in revealing the fraction of the indentation re-

sistance attributable to plastic straining for the various materials furnishes a most interesting index to their "work hardenability."

A better choice of term than "absolute hardness" for these special measurements might be advisable. The term "unworked indentation resistance" would be more suggestive of the actual process involved in the measurement and avoids the controversy over a definition of hardness. Resistance to indentation under the actual conditions of plastic straining which usually accompany the process of indentation is but one of the concepts of hardness that has been found useful. Unworked indentation resistance constitutes a rather special case of hardness not to be confused with the workaday understanding of hardness; nevertheless, it is an attribute of metals whose value is of importance to a broad understanding of hardness.

The authors make the tacit assumption that the value which they term "absolute hardness" is independent of the diameter of indentation. It would be most illuminating, however, to see their measurements extended over ranges of indentation diameters and for different diameters of ball. Such measurements would serve to substantiate definitely the expression in the second line on page 352 that $P_A = a_A d^2$.

Granting that $P_A = a_A d^2$ is a correct relationship pertaining to "absolute hardness," the mathematical development which the authors give on page 352 does not seem consistent with the known facts about the Meyer equation, $P_M = a_M d^n$. In this equation the magnitude of the constant a_M is dependent upon the particular diameter of the ball used, as well as the properties of the metal.

In O'Neill's book, referred to by the authors, is given on page 50 a discussion of the effect of ball diameter showing that the Meyer a_M decreases as the ball diameter increases. From the data there given it may be shown that a_M is dependent upon the Meyer n as well as the ball diameter, D :

$$a_M = \frac{a_o}{D^{n-2}}$$

where a_o is a constant having the same dimensions as the Meyer hardness number, differing from it by the factor $\frac{4}{\pi}$,

$$M = \frac{4}{\pi} a_o = \frac{4}{\pi} a_M D^{n-2}$$

In the case of the equation for unworked metal, the constant a_A is presumed to be an intrinsic value for the material, independent of size or shape of the indenting tool. Studies which H. J. Sprengel and the writer have made on indentations "stress relieved" in vacuo indicate the same approximate value for "absolute hardness" whether a ball or Vickers pyramid be the indenter. It then follows that a_A and a_M are intrinsically and numerically different values and it is difficult to understand the basis upon which the authors adopt the equation on page 352, line 6, where $\frac{M}{A} = d^{n-2}$, instead of $\frac{M}{A} = \frac{a_M}{a_A} d^{n-2}$.

Aside from the fact that no numerical coincidence is to be expected between a_A and a_M, it should be recognized that these two constants are measures of intrinsically different effects. Constant a_A is clearly a parameter of what the authors term "absolute hardness," whereas a_M is a parameter of the sum of the absolute hardness and the resistance incident to strain hardening. It is quite apparent then that, since two independent parameters are involved, three constants are needed to express the Meyer number in terms of diameter of indentation and that a single determination of each M and A will not suffice to fix the value of n, which is quite clearly shown by an examination of the values in the right-hand column of the authors' Table III.

The authors might not have fallen into the error under discussion if a more rational equation than the one proposed by Meyer were in vogue for expressing the relationship between the loads and the dimensions of ball indentations. The Meyer equation is purely empirical and its constants have no definite dimensional significance. Physical significances usually ascribed to its constants are rather nebulous. It is thoroughly feasible, however, to write another equation, in terms of measurements such as the authors make, in which the constants have the same dimensional significance as the physical quantities measured.

The difference between M and A defines the resistance directly attributable to the strain hardening, S.

$$S = M - A$$

Since we have granted that A depends only upon a constant ratio between load and diameter it remains to define a function for S in terms of diameter. It has been demonstrated that strain hardening can be expressed in terms of either diameter of indentation or applied load. We may therefore write that

$$M = A + f_1(d)$$

$$\text{or,} \quad M = A + f_2(P)$$

In the Meyer equation no discrimination is made between the absolute hardness constant and that arising from the strain hardening component of the resistance. For this reason, the dimensional significance of the constant a_M has been somewhat obscure.

As good an approximation to the data as found using the Meyer equation is obtained using either of the following types of expression:

$$M = A + S_d \log \left(\frac{d}{d_o}\right)$$

$$\text{or,} \quad M = A + S_P \log \left(\frac{P}{P_o}\right)$$

where S_d and S_P are strain hardening constants having the same dimensions as hardness numbers M and A. There is considerable theoretical justification for assuming that strain hardening is a logarithmic function of increasing indentation. If we consider the strain hardening capacity of the metal to be limited, it is natural to expect that as indentation proceeds it will face a law of diminishing returns as far as its effectiveness in producing increase of hardening is concerned. The logarithmic function expresses just such a circumstance. The constants d_o and P_o may be considered as the contact diam-

eter and its load at which there commences sufficient plastic deformation to produce strain hardening. It then follows that:

$$\left(\frac{d}{d_o}\right)^{S_D} = \left(\frac{P}{P_o}\right)^{S_P}$$

Solving for P it follows that:

$$P = d_o^{\frac{P_o}{S_D/S_P}} \times d^{S_D/S_P}$$

which is seen to be the same form as the Meyer equation. The ratio S_D/S_P is then equal to n and the Meyer a_M is identical with $d_o^{\frac{P_o}{S_D/S_P}}$. Since, then, by definition:

$$a_M = \frac{P_o}{d_o^n}, \text{ and the assumption be made that } a_A = \frac{P_o}{d_o^2}$$

it furthermore follows that:

$$\frac{a_M}{a_A} = d_o^{n-2}$$

$$\text{or,} \qquad d_o = \left(\frac{a_A}{a_M}\right)^{n-2}$$

and thus definite dimensions are assigned to the Meyer constants. The Meyer equation is thus another form of expressing the diminishing strain hardening capacity above P_o and d_o in the same sense as that for the logarithmic equations.

If the measurements from two Brinell impressions at different loads are available, the values of the strain hardening constants may be calculated as follows:

$$S_D = \frac{M_2 - M_1}{\log d_2 - \log d_1}$$

$$S_P = \frac{M_2 - M_1}{\log P_2 - \log P_1}$$

$$\frac{S_D}{S_P} = \frac{\log P_2 - \log P_1}{\log d_2 - \log d_1} = n$$

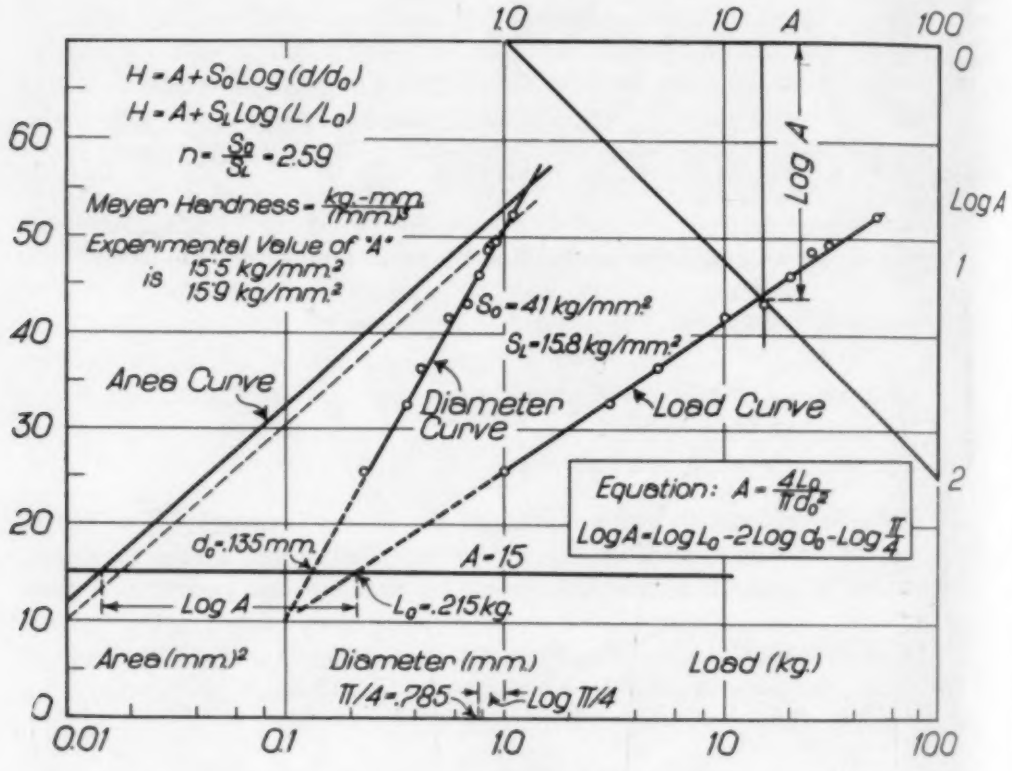
Making use of the assumption that the absolute hardness may be represented in terms of P_o and d_o, we may write that:

$$M\left[1 - \left(\frac{d_o}{d}\right)^{n-2}\right] = S_D \log \frac{d}{d_o}$$

$$M\left[1 - \left(\frac{P_o}{P}\right)^{\frac{n-2}{n}}\right] = S_P \log \frac{P}{P_o}$$

Since S_D, S_P, and n may be computed, values for d_o and P_o which satisfy these equations may be found. This is accomplished most conveniently by graphical solution upon semilogarithmic plots of d and P as functions of M. This solution thus yields a theoretical derivation of "absolute hardness" from the data

upon the metal under strain hardening conditions of test. The accompanying chart illustrates the method as applied to annealed copper. The theoretically computed value of absolute hardness for the copper is in good agreement with the experimental value as determined by either the "removal" method of Messrs. Mahin and Foss or by the stress-relieving technique employed by Mr. Sprengel



Theoretical Absolute Hardness Determination for Copper (Annealed).

and the writer. It would be most interesting if the authors made available more of their Brinell indentation measurements so that the theoretical values of absolute hardness could be computed for comparison with the experimental determinations.

Written Discussion: By R. H. Heyer, junior metallurgist, and R. L. Kenyon, research metallurgist, American Rolling Mill Co., Middletown, Ohio.

The constant flow of papers on hardness testing for the past two or three decades is ample evidence of the importance of this subject. The particular phase of the subject discussed by the authors of this paper is at once perhaps the most interesting and the most difficult to solve of the various problems having to do with hardness testing.

The hardness test, like a number of other widely used tests, is highly empirical and measures some combination of properties of the material being tested. These empirical tests are intended to furnish a relative measure of the behavior of material in a manner which can be correlated with their performance in practical operations. They were never designed to measure "absolute" properties and practically all efforts to eliminate the complicating vari-

ables and reduce them to such fundamentals have proved fruitless. When such properties are to be measured, it seems to be much better to design special tests than to try to adapt old ones.

The authors have pointed to the greater significance of the "yield strength" of materials than their "breaking strength," "tensile strength," or "ultimate strength." This is generally conceded as far as yield strength in tension is concerned and this property is now widely used in engineering design. The authors' definition of "absolute hardness" really corresponds to yield strength in compression. Its determination could be made much more accurately in the standard compression tests than under a spherical ball as in an indentation hardness test.

The authors make no claims for their method as suitable for production testing and state that its chief application lies in a study of the fundamental properties of metals and alloys. The paper will now be considered from this standpoint.

Although the authors have used a very ingenious method to separate the effect of work hardening from the hardness test, they have not confined their analysis to measurement of the "absolute hardness," which is their stated problem, but have gone on in an attempt to measure the capacity for work hardening without permitting any work hardening to take place. It is admitted that the yield strength should be determined as the maximum stress which produces no plastic deformation (theoretically, at least) but it seems paradoxical to try to measure work hardening rate without having any work hardening to observe.

According to page 348, the "absolute hardness" is computed from the diameter of the depression which supported the loaded ball without deformation. Presumably the constants a and n also should be calculated from these readings—using at least two and preferably several different loads, the same as in the Meyer analysis of the regular Brinell test.

The authors, however, have used another method of calculation on pages 351 and 352, the basis of which seems unjustified. On page 352, it is stated that "For absolute hardness $P_A = ad^2$." This is apparently based on the assumption that since no deformation has been permitted under the conditions of test there has been no work hardening and that n is therefore equal to 2.0. However, the problem is to determine n and it is therefore begging the question to assume any particular value for it beforehand.

This same assumption has also led to what seems to be an error in computing the values of a from the absolute hardness determination, for on page 352 it is stated that $A = \frac{4a}{\pi}$ which is only true if $n = 2.0$. However, Table III shows that n is definitely not equal to 2.0. In reality $A = \frac{4\,ad^{n-2}}{\pi}$, but it is easier to compute a by substituting n in Meyer's equation $P = ad^n$.

To carry out properly the computation of n and a for the "absolute hardness" test conditions it is necessary to have the data for size of impression under two or more loadings the same as for the Meyer analysis of the regular

Brinell test. There is only one material for which results are given in Table II for more than one load. This is material 9a.

Using the average of the four impressions under 500 kilograms as one loading condition and the single impression under 1000 kilograms as the other, substitution in the formulae,

$$n = \frac{\log P_1 - \log P_2}{\log d_1 - \log d_2} \text{ and } a = \frac{P}{d^n}$$

gives n = 2.22 and a = 23.2.

The values of $n = 2.47$ and $a = 34.0$ for material 9a in Table III would seem to be incorrectly computed. In view of what has been said about yield strength, it is interesting to note that the value of $a = 23.2$ is equivalent to 42,000 pounds per square inch average unit stress based on the projected area of the impression. This is considerably above the nominal yield strength for material of this composition and treatment. This confirms the well known fact that the stress distribution under the ball is not sufficiently simple to permit the use of the projected area for direct calculation of stress.

The discovery of these discrepancies in the calculation of a and n from the absolute hardness test led to an inspection of the corresponding values computed from the Meyer numbers obtained from regular Brinell impressions. Here again the only case in which sufficient data were given was for material 9a. Using the average of the four impressions under 500 kilograms as one condition and the single impression under 1000 kilograms as the other, and substituting in the same formulae as before gives $n = 1.93$ and $a = 71.2$. These results do not agree with the values of 2.42 and 43.2 given in Table III for these constants and raises a question as to the method followed by the authors in obtaining the results presented in this table.

A detailed comment on the conclusions drawn by the authors will be omitted in view of the apparent need for recomputing Table III. Practical experience raises some question as to the validity or at least the general application of the statements regarding the lack of relationship between grain size and rate of work hardening. Observations in many operations involving plastic deformation indicate that fine-grained materials cold work faster than coarser grained specimens of the same material. Conclusion number 2 on page 352 seems to be entirely unfounded as has been shown.

In spite of the criticisms that have been made, it is believed that this method offers the best approach yet offered to the "absolute hardness" when defined as "the maximum unit stress which a material will support without permanent indentation." The use of a number of different loads in carrying out the Meyer analysis is recommended and it is hoped that the authors will extend their investigations to include cold-worked as well as annealed materials.

Authors' Reply

Mr. Kanter suggests that the term "absolute hardness" is not the best that could be devised to indicate the property discussed in this paper and he proposes "unworked indentation resistance" as more appropriate. The authors entertain no prejudice in this connection, remarking simply that the original term has been in use for a long time and that it seems doubtful whether the

longer expression will come into general use, even though it is undoubtedly more definitely expressive.

Mr. Kanter also raises the theoretical objection that our equation expressing the ratio of Meyer hardness number to absolute hardness is based upon the incorrect assumption that while the Meyer a is independent of ball diameter for absolute hardness it varies with ball diameter for Meyer hardness, so that the equation $\frac{M}{A} = d^{n-2}$ should be $\frac{M}{A} = \frac{a_M}{a_A} d^{n-2}$. This criticism appears to be valid and when we have accumulated sufficient data for the determination of a_M for various ball diameters we should be able to recalculate our results upon the new basis. Since the 10-millimeter ball was used in all determinations reported for this investigation the values for Table III will, presumably, be changed somewhat.

The new formulas proposed by Mr. Kanter for calculating strain hardening constants is interesting and it appears to be based upon logical assumptions and derivations. The authors will gladly supply their own experimental data for use in checking these formulas. (See the reply to the discussion by Heyer and Kenyon.)

The discussion offered by Messrs. Heyer and Kenyon contains a number of points upon which the authors of this paper must disagree. Heyer and Kenyon observe that "the authors' definition of absolute hardness really corresponds to yield strength in compression. Its determination could be made much more accurately in the standard compression tests than under a spherical ball as in indentation tests." It is difficult to understand how such a statement as is quoted above could be made by anyone who is at all familiar with physical testing methods and with their interpretation. Absolute hardness does not correspond with yield strength in compression, any more than conventional hardness (involving strain hardening) corresponds with ultimate strength. The authors mentioned these values in the paper but only to illustrate, in a qualitative way, their relative usefulness to the designing engineer. It seems useless to elaborate upon the fundamental difference between yield strength, as measured in compression tests, and absolute hardness. It may be pointed out, merely, that in compression tests standard pieces, unsupported at the sides, are tested while in any hardness test the entire supporting mass of metal comes into play. This, it would have seemed, is common knowledge among those who perform physical tests of metals or other materials.

Messrs. Heyer and Kenyon state also that "it is paradoxical to try to measure work hardening rate without having any work hardening to observe." The authors have made no such "paradoxical" attempt. All deductions concerning work hardening characteristics have been made by comparing determinations of Meyer hardness numbers and absolute hardness. The statement of Heyer and Kenyon that "presumably the constants a and n also should be calculated from these" (absolute hardness?) "readings—using at least two and preferably several different loads" appears equally pointless. Obviously the equation $n = \frac{\log P_1 - \log P_2}{\log d_1 - \log d_2}$ is not applicable to direct absolute hardness de-

terminations, in which determinations no strain hardening takes place and in which n therefore represents a quality which does not come into play.

The discovery of an apparent error in the calculation of a and n from Brinell impressions made under different loads constitutes legitimate ground for criticism and it calls for an explanation. The Meyer hardness results obtained by various loadings were not reported in the paper, in the interest of space saving. However it should have been explained that we did not actually substitute values of log P_1 and log P_2 in the equation shown above, following instead the usual procedure of plotting P and d values on log-log paper and using the slope of the line as the value for n. Although this is commonly accepted procedure, mention should have been made of it in the paper. Since certain experimental errors enter all such determinations, not all of the determined points will fall exactly upon the indicated graph. But, even at this date, the authors do not know why they happened to throw the one determination (for specimen 9a) into Table II and it is especially unfortunate that this one determination, reported for the 1000-kilogram load, fell away from the straight line. The criticism offered by Heyer and Kenyon is therefore apparently justified by the published table, even though a reproduction of the graph used would have answered the criticism.

These experimental values and the accompanying log-log graphs probably should have been included in the original paper. As they were not, it is hoped that they may logically be included in some future report in connection with the continuation of this investigation.

Messrs. Heyer and Kenyon remark also that the conclusion regarding the effect of grain size upon strain hardening seems to be unfounded. If they had carefully read the authors' conclusion in the preprinted paper they would have noted that the authors specifically stated that they do not regard the two experiments involving grain-size differences as conclusive. They merely pointed out that the two experiments did not, in themselves, provide any ground for expecting differences in strain hardening as a result of grain-size differences.

In conclusion, the authors desire to state that this investigation is to be continued and that a very important gain in the rapidity of making tests is to be expected from the use of a hydraulic testing machine, recently installed in the Notre Dame laboratories. Up to this time it has been necessary to proceed, in direct determinations of absolute hardness, from the standpoint of a constant load, forming depressions of the exact diameter required to support this load without involving further inelastic deformation. In the future the experimental method will involve the converse of this procedure. Depressions will be formed, within any suitable range of diameters, the optimum load then being experimentally determined. Following this procedure it should be possible to obtain experimental data much more rapidly and with less tedious manipulation. It is expected also that we shall be able to extend direct determinations of absolute hardness to harder alloys. This will be possible only when suitable tools for cutting depressions are available. Through the interest expressed and the courtesy extended by Mr. C. B. Sadtler, metallurgist for Barber-Colman Company, special forming tools and penetrators tipped with cemented tungsten carbide are being fabricated. When these tools and penetrators become available, interesting and, it is hoped, profitable lines of investigations will be opened.

RELATION BETWEEN THE ROCKWELL "C" AND DIAMOND PYRAMID HARDNESS SCALES

By Howard Scott and T. H. Gray

Abstract

Because of inconsistent published data on the relation of Rockwell "C" to diamond pyramid hardness and the need for an accurate conversion table, a careful study of this relation was made. Eliminating various sources of error, consistent data were obtained on hardened steels which showed that the relation is independent of steel composition. A conversion table based on these observations is given.

Investigating the theoretical relation of Rockwell "C" to diamond pyramid hardness developed by Petrenko, it was found that the major factor preventing concurrence of the calculated and observed data is elastic recovery or spring-back of the metal under the impression. The amount of this recovery was found to vary with hardness from 0.0005 to 0.0008 inch, being a maximum at 45 RC. It amounts to 15-20 per cent of the impression depth and is, therefore, an important variable in the Rockwell test.

Introduction

THE metallurgical fraternity is quite familiar with the confusion, troubles and irritation arising from the general use of two temperature scales. Nevertheless, it tolerates no less than 5 hardness scales despite the fact that hardness is the subject of as much or more concern than temperature. The question therefore arises: Is this condition necessary? If not, how can it be corrected? Seeking an answer to the first question, the work reported here was undertaken. If it is not a necessary consequence of the nature of hardness or of hardness testing instruments, the technical answer to the second question is quite obvious.

The obvious means for eliminating all but one hardness scale is to convert each hardness observation on another scale to the equivalent value on a reference scale. Certain instrument makers

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have conceded the desirability of so doing by marking their instrument with a reference scale as well as their own arbitrary scale. There is a large number of conversion tables in current use which suggest that this is an entirely legitimate thing to do. Examining tables from different sources, however, one finds discrepancies so large that the possibility of accurate conversion seems quite doubtful. If these discrepancies are due simply to experimental errors or neglect of some essential precaution, they can be easily rectified. If, however, they are due to differences in materials brought out by different actions in the several instruments compared, the problem becomes rather complicated and an answer is hedged by objectionable restrictions. Nevertheless, the possibility of a favorable answer seemed good, so work was undertaken on one phase of the problem at the specific request of our Inspection Department.

The basis for the experimental work described here is brought out in a brief discussion of the three principal hardness testing machines, namely, the Brinell, Rockwell and Vickers. These are all dead load hardness tests to which consideration is restricted. The original dead load hardness test is that of Brinell. A hardened steel ball is pressed into the work under a measured load and the diameter of the permanent impression made is measured. From these observations and the ball diameter, the Brinell hardness number (BHN) is calculated assuming that the impression is spherical and has the same radius as the steel ball.

The machines in general use for making this test are of simple construction affording little opportunity for error due to defective action. They are easily calibrated by checking the load applied, diameter of ball used and device used for measuring the impression diameter.

By definition, the Brinell hardness number, BHN, is the load on the ball in kilograms divided by the spherical area of the impression in square millimeters. If our measurements and calculations are correct, we should have the true Brinell hardness of the piece tested. Actually, the number obtained varies materially with the load applied and with the diameter of ball used. Usually these variables are held constant at 3000 kilograms and 10 millimeters respectively and still inconsistencies are noted, particularly at high hardness values, due to deformation of the ball. This last error may be avoided when using the standard hardened steel ball by restricting tests to metals under 450 BHN. A mechanical limitation is met at the lower end of

the hardness scale so that metals under about 70 BHN cannot be tested with the load and ball diameter mentioned. So restricted, the Brinell scale is too short to be considered as a reference scale of hardness.

The Rockwell hardness testing machine met the demand for a reliable test for metals of high hardness. Discrepancies in conversion relations are greatest at high hardness and this instrument with the diamond cone and 150 kilograms load, C- scale, is most widely used for tests at high hardness, so it was one of the pair selected for the study of the conversion relations considered here. Being more complicated than the Brinell test, it is not as easily standardized by reference to fundamental standards of length and weight. On this account, the maker supplies standardized test blocks for checking the instrument. Obviously, it is desirable to standardize these blocks by some test that may be easily calibrated from fundamental standards, which is another reason for the present comparison.

With the Rockwell test, the Brinell principle of expressing hardness as unit pressure is discarded, the Rockwell hardness scale reading being proportional to depth of impression. On this account, one point difference in Rockwell hardness is equivalent to a much larger difference in Brinell hardness at high hardness values than at low. The equivalent Brinell hardness can nevertheless be calculated from the scale reading and constants of the machine. This is done here and the results compared with the experimentally determined relation.

The diamond pyramid hardness test introduced by Vickers, Ltd., is free from the objections mentioned to both the Brinell and Rockwell tests. Like the Rockwell test, it uses a diamond penetrator and is therefore applicable to the hardest metals. Hardness is expressed as in the Brinell test by load per unit area and identified by DPH (diamond pyramid number). Hardness variations due to change of load or size of ball inherent in the Brinell test are eliminated by use of the pyramid shape indenter. There is no limitation at the lower end of the hardness scale, the same machine serving, with change of load or magnification of impression, to cover the range in hardness from tin, 5 DPH, to tungsten carbide, 1500 DPH, at least.

The undistorted hardness scale provided by the Vickers test, combined with its adaptability to direct calibration, identify it as the ideal scale for use as a reference standard. Although an admirable laboratory tool, it is not well adapted to routine testing so direct com-

parison of hardness observations made with the more practical Rockwell test is all the more desirable.

To make an accurate comparison, it is necessary that the tests be made on carefully standardized machines and that all known possible sources of error be eliminated. What was done in this direction to assure accurate observations is described in the next section.

Experimental Technique

Rather than undertake standardization of our particular Rockwell machine which is quite old, test blocks prepared in our laboratory were submitted to the maker of the instrument for test. The tests were cordially made by the Wilson Mechanical Instrument Company and are recorded here as the true Rockwell "C" hardness of the test blocks. Repeat tests were made by us on the same blocks with a new Rockwell machine, Model 3-R, the values from which did not depart from the maker's observations by more than ½ point Rockwell "C".

Diamond pyramid hardness tests were made with the Vickers hardness testing machine in our laboratory. Each factor determining the hardness number was checked against fundamental standards. Angles on the diamond penetrator were measured on a Zeiss Universal Micro Measuring Machine. The 136-degree angle between opposite sloping faces was correct within one minute of arc and these faces intersected in a sharp point. The lever arm was measured and found to have a ratio of 20:1 within one per cent. The weights were checked and found to vary not more than 0.4 per cent from 1/20 of the indicated load. To check on friction in the mechanism, the actual load on the penetrator was measured and found to be within one per cent of the indicated value which is the accuracy of our available checking equipment.

The micrometer microscope was checked against ruled lines 0.1 millimeter apart on a glass plate with the ⅔-inch objective used exclusively for tests on hard metals. Dimensions in millimeters are obtained from the microscope scale reading by multiplying it by the factor 0.002. The glass reference plate was in turn compared with a certified length standard by means of the Zeiss Universal Machine. No error larger than 0.01 per cent at 10 millimeters was found.

Various precautions were observed in using the Vickers machine. The dash pot controlling the loading cycle was maintained full of oil

to avoid impact loading. The loading cycle was adjusted for 10 seconds complete release of load. Lost motion in the microscope micrometer was held constant by always bringing the knife edges in toward the impression for a reading. The microscope was adjusted so the knife edges were strictly parallel to a diagonal of the impression and the zero position checked. Both diagonals were measured and the mean value taken as a single hardness observation, differences being kept very small by keeping the test surface strictly in a plane perpendicular to the axis of the penetrator. There was some difference between observations by different uninstructed observers, but with instructions, checks within 6 points DPH at 790 DPH were easily obtained. The laboratory Vickers machine agreed within a few points with another machine in the plant.

The test blocks used here were specially prepared and represent a wide range of steel compositions and 12 different analyses. They were surface ground ¼ inch thick to have both sides parallel and had an area of at least 2 square inches. Each set of a particular composition was quenched to a uniform hardness then tempered to several hardness values from 260 to 1000 DPH (23-70 RC), Table I. Six Rockwell tests and nine Vickers tests were made on each block, the mean values of each set of readings being given in the table.

An essential requirement of test blocks for this work is that they have uniform hardness. This characteristic was evaluated by calculating the mean departure from the mean of each set of readings, namely, the average of the differences between the individual readings and the mean. It is given after the ± signs in Table I. The values show a remarkably high degree of uniformity in both Rockwell and Vickers tests, the mean departure being less than 0.5 per cent in almost all cases.

This high degree of uniformity was obtained by special precautions in heat treatment. The blocks were hardened by heating in a protective atmosphere followed by quenching for completely martensitic hardening. After tempering, the blocks were carefully polished so that a clean-cut impression was obtained. The shallow diamond pyramid tests were made at several levels below the as-quenched surface to assure absence of decarburization.

The diamond pyramid tests for comparison were all made with a 50-kilogram load in order to secure maximum accuracy. According to the principle of design, readings made with other loads should be identical. To test this point, tests were made on a number of

Table I

Composition, Heat Treatment and Hardness of Test Blocks Used in Comparison of Rockwell "C" and Diamond Pyramid Hardness

Block No.	Nominal Composition Per Cent C	Cr	V	X	Y	Quenching Temp. Degrs. Cent.	Medium	Tempering Temp. Degrs. Cent.	RC (150 kg.)	DPH (50 kg.)
G 6	1.1	...	...	...	...	800	Water	25	68.5 ± 0.3	902 ± 6
3	1.1	...	...	...	...	800	Water	130	67.0 ± 0.2	862 ± 2
G 3	1.1	...	...	...	...	800	Water	230	62.7 ± 0.2	753 ± 5
G 4	1.1	...	...	...	...	800	Water	330	55.0 ± 0.1	586 ± 1
G 7	1.1	...	...	...	...	800	Water	435	47.5 ± 0.1	468 ± 1
G 5	1.1	...	...	...	...	800	Water	500	45.2 ± 0.2	439 ± 2
R 1	0.95	0.5	0.15	...	...	Rockwell Test Blocks			65.8 ± 0.2	794 ± 2
R 2	0.95	0.5	0.15	...	...				62.9 ± 0.1	731 ± 3
R 3	0.95	0.5	0.15	...	...				59.2 ± 0.2	673 ± 3
R 4	0.95	0.5	0.15	...	...				45.0 ± 0.1	439 ± 2
R 5	0.95	0.5	0.15	...	...				38.4 ± 0.4	375 ± 2
R 6	0.95	0.5	0.15	...	...				25.9 ± 0.2	267 ± 2
U 4	1.0	5.0	0.2	1.0 Mo	...	940	Air	25	66.0 ± 0.0	816 ± 1
U 6	1.0	5.0	0.2	1.0 Mo	...	940	Air	175	62.7 ± 0.3	746 ± 4
U 3	1.0	5.0	0.2	1.0 Mo	...	940	Air	200	62.0 ± 0.1	712 ± 2
U 8	1.0	5.0	0.2	1.0 Mo	...	940	Air	500	57.8 ± 0.2	623 ± 3
U 5	1.0	5.0	0.2	1.0 Mo	...	940	Air	600	51.3 ± 0.2	531 ± 3
U 7	1.0	5.0	0.2	1.0 Mo	...	940	Air	650	45.7 ± 0.4	447 ± 2
B 1	1.6	12.0	0.15	0.8 Mo	...	1030	Oil	25	65.2 ± 0.4	803 ± 5
B 2	1.6	12.0	0.15	0.8 Mo	...	1030	Oil	200	65.0 ± 0.3	759 ± 4
B 3	1.6	12.0	0.15	0.8 Mo	...	1030	Oil	350	59.0 ± 0.0	663 ± 2
B 4	1.6	12.0	0.15	0.8 Mo	...	1030	Oil	650	51.7 ± 0.2	554 ± 3
1 C 5	0.5	1.0	0.15	...	...	860	Water	25	63.2 ± 0.3	749 ± 6
1 C 2	0.5	1.0	0.15	...	...	860	Water	220	62.7 ± 0.1	734 ± 15
1 C 1	0.5	1.0	0.15	...	...	860	Water	300	61.7 ± 0.8	712 ± 11
1 C 6	0.5	1.0	0.15	...	...	860	Water	425	51.2 ± 0.3	510 ± 4
1 C 4	0.5	1.0	0.15	...	...	860	Water	500	44.0 ± 0.2	416 ± 3
C 7	0.4	1.5	...	3.5 Ni	...	820	Oil	25	56.0 ± 0.0	623 ± 3
C 8	0.4	1.5	...	3.5 Ni	...	820	Oil	200	52.2 ± 0.2	551 ± 2
C 2	0.4	1.5	...	3.5 Ni	...	820	Oil	400	42.2 ± 0.3	426 ± 6
C 6	0.4	1.5	...	3.5 Ni	...	820	Oil	500	40.2 ± 0.2	388 ± 2
S 5	0.7	0.8	0.2	...	...	820	Water	25	66.5 ± 0.1	867 ± 4
S 7	0.7	0.8	0.2	...	...	820	Water	130	64.6 ± 0.3	795 ± 6
S 3	0.7	0.8	0.2	...	...	820	Water	200	60.2 ± 0.2	695 ± 4
S 8	0.7	0.8	0.2	...	...	820	Water	250	53.0 ± 0.2	564 ± 4
S 4	0.7	0.8	0.2	...	...	820	Water	450	47.0 ± 0.1	466 ± 3
S 6	0.7	0.8	0.2	...	...	820	Water	500	45.3 ± 0.2	447 ± 2
V 5	1.2	0.4	0.2	1.5 W	...	860	Water	25	69.0 ± 0.2	912 ± 3
V 5	1.2	0.4	0.2	1.5 W	...	860	Water	130	67.6 ± 0.2	877 ± 3
V 6	1.2	0.4	0.2	1.5 W	...	860	Water	225	64.2 ± 0.2	767 ± 3
V 4	1.2	0.4	0.2	1.5 W	...	860	Water	300	59.5 ± 0.0	662 ± 2
V 7	1.2	0.4	0.2	1.5 W	...	860	Water	500	52.0 ± 0.1	520 ± 3
O 4	1.4	0.5	...	4.0 W	0.5 Mo	800	Water	25	68.0 ± 0.2	909 ± 3
O 5	1.4	0.5	...	4.0 W	0.5 Mo	800	Water	130	67.5 ± 0.2	878 ± 2
O 2	1.4	0.5	...	4.0 W	0.5 Mo	800	Water	310	61.3 ± 0.2	719 ± 3
O 3	1.4	0.5	...	4.0 W	0.5 Mo	800	Water	350	58.7 ± 0.2	660 ± 3
O 1	1.4	0.5	...	4.0 W	0.5 Mo	800	Water	450	53.5 ± 0.2	581 ± 3
A 7	0.4	3.5	0.7	14 W	...	1030	Oil	25	49.5 ± 0.2	492 ± 3
A 1	0.4	3.5	0.7	14 W	...	1030	Oil	650	45.1 ± 0.1	449 ± 3
A 8	0.4	3.5	0.7	14 W	...	1030	Oil	800	32.0 ± 0.2	316 ± 2
A 2	0.4	3.5	0.7	14 W	...	1030	Oil	700	23.2 ± 0.2	258 ± 1
W 1	0.7	4	1.0	18 W	...	1280	Oil	25	65.3 ± 0.2	814 ± 5
W 3	0.7	4	1.0	18 W	...	1280	Oil	467	64.8 ± 0.3	795 ± 5
W 2	0.7	4	1.0	18 W	...	1280	Oil	345	61.7 ± 0.4	721 ± 5
W 5	0.7	4	1.0	18 W	...	1280	Oil	677	55.2 ± 0.3	603 ± 6
M 2	0.9	4	...	2 W	36 Co	980	Oil	550	70.5 ± 0.0	999 ± 4
M 1	0.9	4	...	2 W	36 Co	980	Oil	25	65.6 ± 0.3	812 ± 4

Table II

Comparison of Diamond Pyramid Hardness Values Made With Different Loads

Block No.	Diamond Pyramid Hardness for Load of: 50 kg.	30 kg.	10 kg.	Differences 50-30 kg.	50-10 kg.
G 6	902 ± 6	897 ± 3	898 ± 4	+ 5	+ 4
G 3	753 ± 5	755 ± 6	748 ± 7	− 2	+ 5
G 4	586 ± 1	588 ± 3	592 ± 5	− 2	− 6
G 7	468 ± 1	470 ± 2	468 ± 4	− 2	0
U 4	816 ± 1	810 ± 5	796 ± 6	+ 6	+ 20
U 3	712 ± 2	707 ± 5	702 ± 5	+ 5	+ 10
U 5	531 ± 3	530 ± 3	527 ± 5	+ 1	+ 4
B 1	803 ± 5	797 ± 5	798 ± 8	+ 6	+ 5
B 2	759 ± 4	757 ± 6	756 ± 7	+ 2	+ 3
B 3	663 ± 2	664 ± 3	659 ± 5	− 1	+ 4
B 4	554 ± 3	557 ± 3	561 ± 7		
C 7	623 ± 3	625 ± 5	628 ± 6	− 2	− 5
C 8	551 ± 2	560 ± 5	559 ± 7	− 9	− 8
C 2	426 ± 6	430 ± 7	429 ± 9	− 4	− 3
C 6	388 ± 2	394 ± 2	392 ± 3	− 6	− 4
S 5	867 ± 4	866 ± 6	874 ± 7	+ 1	− 7
S 3	695 ± 4	691 ± 4	700 ± 8	+ 4	− 5
S 8	564 ± 4	565 ± 5	565 ± 5	− 1	− 1
S 6	447 ± 2	449 ± 2	448 ± 4	− 2	− 1
V 1	878 ± 1	885 ± 4	882 ± 5	− 7	− 4
V 6	767 ± 3	769 ± 7	759 ± 6	− 2	+ 8
V 4	662 ± 2	661 ± 2	656 ± 2	+ 1	+ 6
V 7	520 ± 3	524 ± 2	520 ± 4	− 4	0
4	909 ± 3	916 ± 9	910 ± 9	− 7	− 1
2	719 ± 3	722 ± 5	715 ± 6	− 3	+ 4
3	660 ± 3	658 ± 5	663 ± 6	+ 2	− 3
1	581 ± 3	587 ± 4	588 ± 4	− 6	− 7
			Mean	− 1.0	+ 0.7

Table III

Diamond Pyramid Hardness Values for Various Rockwell "C" Values as Found by Authors Compared with Observations Reported Elsewhere

Rockwell "C" 150 Kg.	Equivalent DPH Reported by: Authors	Sawin and Stachrowski	A.S.M. Handbook
70	975	...	...
68	885	960	1050
66	820	905	960
64	770	850	885
62	725	795	820
60	685	740	765
58	645	688	717
56	610	635	654
54	580	590	615
52	545	555	567
50	515	520	540
48	485	490	505
46	460	465	472
44	435	440	437
42	410	415	420
40	385	395	389
38	...	370	375
36	...	350	350
34	...	330	327
32	...	315	305
30	...	300	287
28	...	285	270
26	...	270	263
24	...	260	248
22	...	245	235
20	..	235	223

blocks at 10 and 30-kilogram loads. The results are given in Table II and show no consistent difference from those obtained with a 50-kilogram load, the average difference being 1 point or less. This is further evidence of no significant decarburization for, if present, the lighter loads would give lower hardness values because of shallower penetration than with high loads.

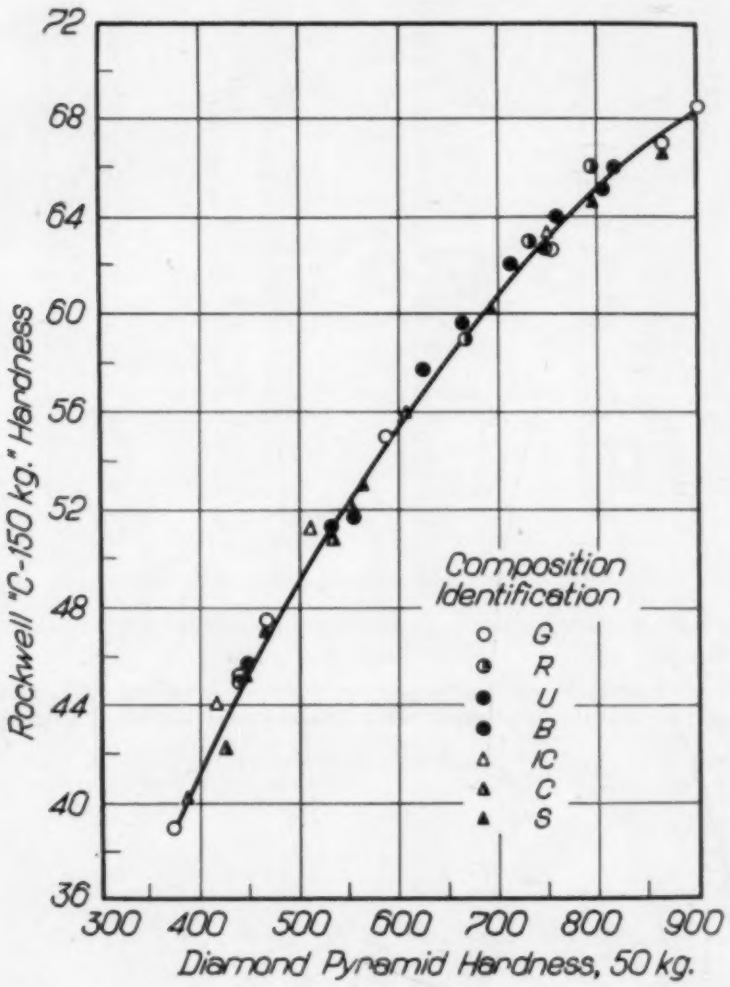


Fig. 1—Relation Between Rockwell "C" and Diamond Pyramid Hardness Obtained on Steels Containing 0 to 12 Per Cent Chromium and Less than 4 Per Cent of Other Alloying Elements.

Observed Conversion Relation

The mean values of Rockwell "C" 150-kilogram hardness are plotted against mean values of diamond pyramid 50-kilogram hardness in Figs. 1 and 2, separation of the steels into two groups being made to avoid crowding. The individual observations all fall within

1 point RC of the curves drawn to represent the average. There is no consistent deviation of any one composition from the curve showing that heat treatment and composition of steel within wide limits does not influence the relation. Also, the curve of Fig. 2 is identical with that of Fig. 1 confirming the absence of a composition or treatment.

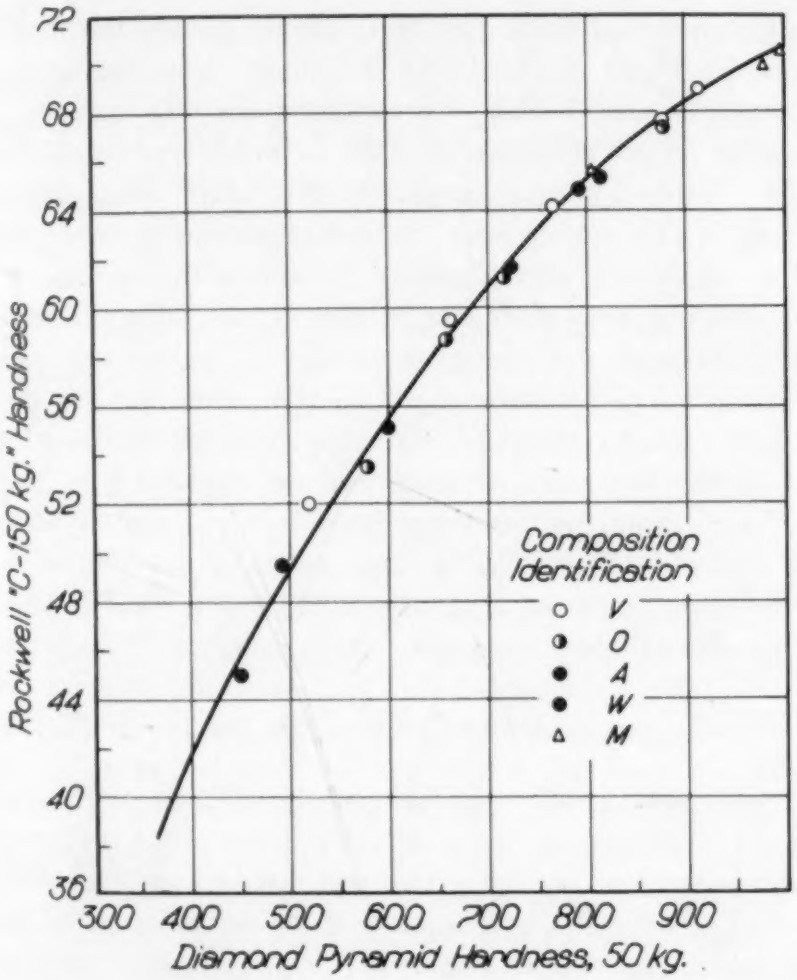


Fig. 2—Relation Between Rockwell "C" and Diamond Pyramid Hardness Obtained on Steels Containing 1 to 18 Per Cent Tungsten and Other Alloying Elements.

This conclusion agrees with that of Sawin and Stachrowski[1] who state: "Rockwell 'C' numbers from 20 to 50 may be converted to Brinell, Vickers and Monotron numbers." Our conversion values, however, differ materially from theirs at high hardness values, Table III. The discrepancy with respect to A.S.M. Handbook values

[1]N. N. Sawin and E. Stachrowski, "Comparative Tests of Hardened Steel by Means of Penetration Testing Apparatus," TRANSACTIONS, American Society for Steel Treating, Vol. 20, 1932, p. 249.

is still greater. At 66 RC Sawin and Stachrowski's value is 85 points DPH high and the Handbook value 140 points high relative to our value of 820 DPH. Below 50 RC the agreement is quite acceptable. It is possible that Sawin and Stachrowski's observations are in error due to failure to refer back to Rockwell hardness standards. The same may be true also of the Handbook relation, though the further possibility exists that there has been double conversion, that is, the relation of Rockwell "C" to DPH is deduced from relations of each to some other hardness scale, thereby compounding errors.

In order to put the data obtained in more convenient form for conversion, Table IV was prepared, the values being taken from Figs. 1 and 2. By taking even steps in diamond pyramid hardness, position in the table is significant as to hardness difference. That is to say values one row apart at the top of the table differ in static penetration hardness by the same amount as values one row apart at the bottom. The ultimate object of this work was, of course, to provide just such an accurate relation so that all hardness readings reported in the literature at least can be expressed in one scale, namely, the diamond pyramid hardness scale, no matter what hardness test is made. This table enables one to do so for the Rockwell "C" hardness readings and it is hoped that further work will be done making possible reliable conversions from other hardness tests.

Calculation of Conversion Relations

The possibility exists of calculating the relation of Rockwell "C" to diamond pyramid hardness already determined experimentally from the constants of the respective test instruments. Petrenko[2] has derived relations for so doing, assuming no deformation of the penetrator or elastic recovery of the work. Applying his equations some interesting facts are disclosed.

Since Petrenko assumes no deformation of the Brinell ball in his equation for the relation of BHN to RC one may substitute DPH for BHN in his equation:

$$DPH = \frac{150}{2\pi r S + 10.882 (L^2 + 21 L)} \qquad (1)$$

which is applicable to RC values of 23 to 80. These symbols are defined by Fig. 3. From the dimensions of the Rockwell penetrator:

[2] S. N. Petrenko, "Relationships Between Rockwell and Brinell Numbers," U. S. Bureau of Standards, Journal of Research, Vol. 5, 1930, p. 19.

$$r = 0.20 \text{ mm.}$$
$$S = 0.0268 \text{ mm.}$$
$$l = 0.0578 \text{ mm.}$$

so — $$DPH = \frac{150}{0.0337 + 10.882\ (L^2 + 0.1155\ L)} \qquad (2)$$

L may be evaluated in terms of RC from two other equations, namely:

$$L^2 + 4.308\ SL + 4.308\ S\ (S - 15\ h_o) = 0 \qquad (3)$$

derived from the ratio of major to minor areas and:

$$0.002\ (100 - RC) = L + S - h_o \qquad (4)$$

derived from the definition of Rockwell "C" hardness. Evaluating constants and combining:

$$L^2 - 1.617\ L + 0.3031 - 0.003465\ RC = 0 \qquad (5)$$

the solution of which is:

$$L = \frac{1.617 + \sqrt{1.403 + 0.01386\ RC}}{2} \qquad (6)$$

The values of DPH calculated from equations (2) and (6) are given in Table V, third column. These values are far from our observed values as Petrenko has already indicated in his discussion of their relation to Brinell hardness. Deformation of the penetrator is not a major cause of this discrepancy because of the use of a diamond. The only other obvious cause is elastic recovery or spring back of the metal under the Rockwell penetrator on release of the load. The load being a maximum at the center of the impression, the elastic recovery should have a much greater effect on hardness numbers obtained from depth readings as in the Rockwell test than on hardness numbers obtained from diameter readings as in the Vickers test. Accordingly, the possibility of such an effect was investigated.

The diameter of Rockwell hardness test impressions both under the minor and major loads was measured with the Vickers microscope micrometer, the results being given in Table VI. From these readings the depth of impression was calculated assuming that the impression has the identical shape of the penetrator thereby obtaining depth values, column 6, comparable to those measured by RC but

unaffected by elastic recovery. The observed Rockwell number gives the depth of impression h_1 as modified by the presumed elastic recovery, column 7, so the difference then, column 8, is the elastic recovery under the point of the Rockwell penetrator.

The depth of the impressions were calculated from the observed

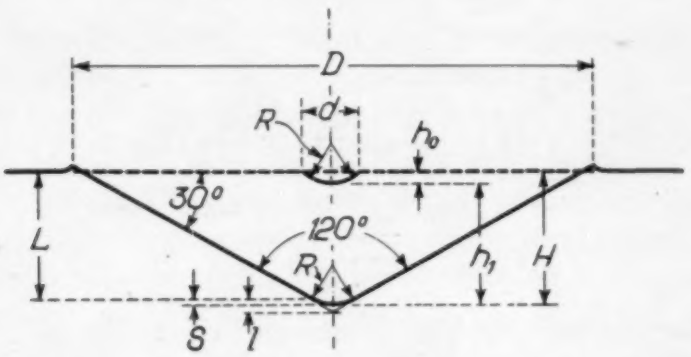


Fig. 3—Geometry of Rockwell Diamond Cone Impression in Work When Impression Has Identical Contour with the Cone. d Represents the Diameter of the Impression Under Minor Load of 10 kg. and D that Under Major Load of 150 kg.

diameters by means of the following relations derived from the geometry and constants of the Rockwell diamond cone:

$$h_0' = 0.20 - \frac{\sqrt{0.16 - d^2}}{2} \qquad (7)$$

$$H' = 0.2887\ D - 0.0310 \qquad (8)$$

where d is the observed diameter of the impression made by the minor load and D that made by the major load. The observed depth of impression h_1 which is that modified by elastic recovery is obtained simply from the definition of Rockwell "C" hardness:

$$RC = 100 - \frac{h_1}{0.002}$$

whence

$$h_1 = 0.20 - 0.002\ RC \qquad (9)$$

The values of elastic recovery are plotted in Fig. 4 against Rockwell "C" hardness. They show a striking phenomenon, namely a peak at about 45 RC. The metal apparently behaves as though it is more plastic both below and above this value. Possibly this value represents maximum toughness of quenched and tempered steel.

Table IV

Conversion Values for Transposing Rockwell "C"—150 Kg. Hardness to Diamond Pyramid Hardness or Vice Versa

DPH (50 Kg.)	RC (150 Kg.)	Depth of Impression in Inches DPH	RC
1000	70.4	1.71×10^{-3}	2.33×10^{-3}
980	70.0	1.73	2.36
960	69.6	1.75	2.40
940	69.2	1.77	2.42
920	68.8	1.79	2.46
900	68.4	1.81	2.49
880	67.8	1.83	2.54
860	67.2	1.85	2.58
840	66.6	1.87	2.63
820	66.0	1.89	2.68
800	65.2	1.92	2.74
780	64.4	1.94	2.80
760	63.6	1.97	2.86
740	62.6	1.99	2.94
720	61.8	2.02	3.01
700	60.8	2.05	3.09
680	59.8	2.08	3.17
660	58.6	2.11	3.26
640	57.6	2.14	3.34
620	56.4	2.18	3.44
600	55.4	2.21	3.52
580	54.2	2.25	3.61
560	53.0	2.29	3.70
540	51.8	2.33	3.80
520	50.4	2.37	3.91
500	49.0	2.42	4.02
480	47.8	2.47	4.11
460	46.2	2.53	4.24
440	44.6	2.58	4.37
420	42.8	2.64	4.51
400	41.0	2.71	4.65

Depth of diamond pyramid 50 Kg. impression $= \dfrac{0.0542}{\sqrt{\text{DPH}}}$

Depth of Rockwell "C—150 Kg." impression $= (7.88 - 0.0788\ \text{RC} \times 10^{-3}$ in.

Table V

Comparison of Observed and Calculated Values of DPH for Several Values of RC

RC	Diamond Pyramid Hardness		
	Observed by Authors	Calculated: Without Correction	Calculated: Corrected for Elastic Recovery
70	975	1537	1248
65	795	1235	969
60	685	984	768
50	515	690	532
40	385	501	399
30	...	379	315
20	...	290	228

It is now a simple matter to correct the calculated relation between DPH and RC of Table V by means of Fig. 4. The values of elastic recovery for each value of RC need only be added to the values of L obtained from equation (6) and substituted in equation

(2). The results of so doing are given in the fourth column of Table V. Still there is a material difference between calculated and observed values at high hardness, but between 60 and 40 RC the agreement is at at least as good as between different conversion relations.

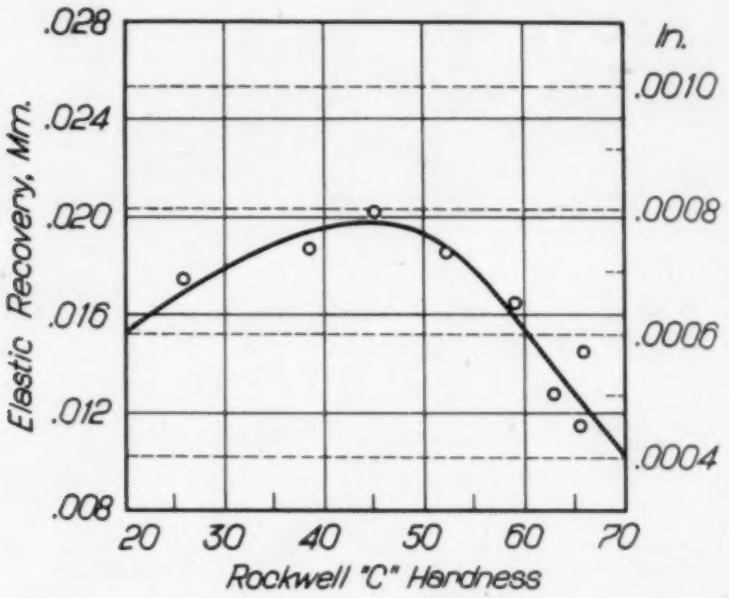


Fig. 4—Elastic Recovery of Work Under Point of Rockwell Diamond Cone on Release of Major Load as Calculated from the Observed Diameters of Major and Minor Impressions and Corresponding Rockwell "C" Number.

Table VI

Calculation of Elastic Recovery During Rockwell "C" Test from Observations on Diameter of Impression Under Major and Minor Loads. All Dimensions in Millimeters.

Observed Rockwell "C" 150 Kg. RC	Observed Diameter of Impression		Calculated Depth of Impression			Observed Depth	Elastic Recovery
	Major D	Minor d	Major H′	Minor h'_o	$H' - h'_o = h'_1$	h_1	$h'_1 - h_1$
66.0	0.431	0.131	0.0935	0.0110	0.0825	0.0680	0.0145
65.8	0.424	0.133	0.0914	0.0115	0.0799	0.0684	0.0115
62.9	0.452	0.140	0.0995	0.0125	0.0870	0.0742	0.0128
59.2	0.494	0.144	0.1116	0.0135	0.0981	0.0816	0.0165
52	0.563	0.161	0.1315	0.0170	0.1145	0.0960	0.0185
45.0	0.634	0.182	0.1520	0.0218	0.1302	0.1100	0.0202
38.4	0.687	0.196	0.1674	0.0255	0.1419	0.1232	0.0187
25.9	0.806	0.229	0.2017	0.0360	0.1657	0.1482	0.0175

Elastic recovery must therefore be considered in any calculation of hardness number on a unit pressure from impression depth readings. The residual discrepancy at high hardness values is a matter for further speculation.

Summary and Conclusions

As part of an effort to provide a means for reporting hardness test observations on different instruments in terms of a single uniform hardness scale, an experimental study was made of the relation between Rockwell "C" and diamond pyramid hardness tests. The tests were made on steel blocks made from a wide range of compositions quenched and tempered to various hardness values. Our results show definitely the absence of any effect of composition or heat treatment on the relation.

Our observed values of diamond pyramid hardness at particular RC values agree well with others reported in the literature at moderate hardness values, but are low at high values. The discrepancy at high values is attributed primarily to failure of other observers to refer back to standards of Rockwell hardness.

Diamond pyramid hardness values were also calculated from Rockwell "C" observations by means of Petrenko's equations and found, as anticipated, to be widely different from the observed values. This difference is attributed to elastic recovery of the metal under the Rockwell penetrator.

Elastic recovery was calculated from observations of diameters of Rockwell impressions and found to be relatively large, ranging from 15 to 20 per cent of the impression depth. It has a maximum values of about 0.0008 inch at 45 RC.

Applying a correction for elastic recovery to the mathematical relation between DPH and RC, the calculated curve was brought into close proximity to the experimental curve in the range 40-60 RC. At higher values there is still considerable divergence, though much less than without this correction.

Acknowledgments

The authors are grateful to J. R. Weaver, Director of the Inspection and Test Department of the Westinghouse Electric and Manufacturing Company, for suggesting and promoting the activity reported here and to V. E. Lysaght of the Wilson Mechanical Instrument Company for his co-operation in making hardness tests and supplying detailed information.

DISCUSSION

Written Discussion: By V. E. Lysaght, Wilson Mechanical Instrument Co., Inc., New York.

The authors are to be complimented on the very thorough and complete paper they have presented.

This discussion of their paper is not intended to indicate approval of the use of conversion charts, none of which are mathematically exact, or can be made mathematically correct. Nevertheless, it must be admitted that conversion tables are used to a large extent and it is gratifying to see a study carried on where the instruments involved have been so carefully checked, the materials upon which the study was made heat treated to insure the maximum uniformity of hardness and the material selected to cover such a wide range of alloys.

The authors have chosen the diamond pyramid hardness scale to be the ideal scale to which all other hardness scales should be referred because they assume this scale provides an undistorted hardness scale and is adaptable to direct calibration.

The above is open to discussion and, furthermore, before any scale is selected as an ideal scale, other factors which enter into the test should be investigated. Many authorities claim it is desirable to report the load at which the determination of the diamond pyramid hardness test is made and if this holds true, although the present study does not bear it out, then the undistorted hardness scale becomes tied up with the load at which the tests were made. No mention is made of the "bulge effect" present in all types of penetration hardness tests. According to O'Neill,[3] in the diamond pyramid hardness test, "piling-up" does not produce a concentric ridge, for while metal is extruded upward along the face of the indenter, it remains practically at the original level near the corners. In such a case, the diagonal measurement gives a low value of both the projected and the contact areas of the indentation and produce erroneously high hardness values. "Sinking-in" gives a partial downward curvature of the metal, causing high values of area and erroneously low hardness numbers. The true area can be determined approximately but for an ideal scale it should be capable of exact mathematical determination.

Is it not extremely pertinent also to ask whether any hardness scale based upon indentation hardness methods could ever be considered "ideal" when "piling-up" around the brink of the impression occurs with some metals and "sinking-in" at the brink occurs with other metals, for piled-up material resists penetration and sinking of the brink facilitates penetration? Such an "ideal" hardness scale would give equal hardness values to metals to which some future method of hardness testing still more "ideal," because not affected by brink characteristics, would not give equal values.

The authors advance, as a possible reason for the lack of agreement between their work and that of previous investigators, the failure of others to refer back to "Rockwell" standards. However, no mention is made of earlier investigators failing to check the diamond pyramid hardness tester, which would involve checking of angle of diamond penetrator, loads, measuring

[3] "The Hardness of Metals and Its Measurement," Sherwood Press, Cleveland.

system, adjustment of micrometer knife edges parallel to diagonal or impression, etc.—a far more complicated requirement than checking a "Rockwell" tester by means of standardized test blocks which all users of the "Rockwell" machine are educated to do. There is good reason to believe that if a round-robin check were made on several diamond pyramid hardness testers, some very interesting results would be obtained.

The unexplained discrepancy between diamond pyramid hardness values obtained from the Vickers tester and from P/A values calculated from the "Rockwell" test may be due to the difficulty of obtaining the true diameter of impression due to "piling-up" effect; and that at high hardness values the shapes of the two indentations are quite dissimilar, one being largely a sphere of definite radius while the other is only defined as a sharp-pointed pyramid.

Oral Discussion

C. B. SADTLER:[4] We have been very much interested and rather vitally concerned in having as close a Rockwell-Vickers conversion relationship as possible, particularly 18-2-1 high speed steel. We attempted five or six years ago to set up such a relationship and felt that we had a fairly good one and we did what the previous discusser considered a desirable thing to do, had something of a "round-robin" check. We took a couple of our Rockwell "C" standard blocks and sent them to the Bureau of Standards and also sent them to another laboratory who we felt were in a position to make both accurate Vickers and Rockwell tests. We obtained a very gratifying agreement. The discrepancies in terms of Vickers' figures were less than ten points, in some cases only two or three points. The Bureau of Standards made three determinations for us and, using that as a standard, the deviation of the other two were within ten points Vickers which we considered good.

More recently we desired to make a further study of the relationship and found that our previous standard was in error by an amount which did not worry us especially although it is more than we like to see. In certain portions of the curve there was as much as 11 points variation from our standard of some five or six years ago. That is nowhere near as bad, however, as the variation which exists between our standards and the ones that are found in various publications. We have assembled data from nine different sources and find the variations are as much as 33 points Vickers below ours to as much as 87 points above ours. Those happen to be the figures at 65 Rockwell "C" equivalent and that is about ten times as bad as what we consider a fair agreement.

It appears that the reference to this paper which was made in a recent issue of *Metal Progress* is somewhat misleading, or as least at variance with observations which we have made in respect to Rockwell and Vickers values for different types of steel. For example, on our standard conversion for 18-4-1 high speed steel, 65 Rockwell "C" is 853 Vickers. On hardened S.A.E. 1095 steel, however, 853 Vickers is 66.5 Rockwell "C."

H. J. FISCHBECK:[5] We have used the Vickers hardness testing machine

[4]Metallurgist, Barber-Colman Co., Rockford, Ill.

[5]Chief metallurgist, Pratt & Whitney Aircraft, East Hartford, Conn.

for over nine years and the Rockwell for 15 years and can therefore agree with the authors that the Vickers makes a better hardness testing machine for laboratory purposes than the Rockwell, but the Rockwell is the better production machine.

We have also not been able to get a true conversion between Vickers and Rockwell. We believe that the reason depends upon, first, the mass of the sample used in the making of the conversion and, second, the finish of the surface. This variation is especially noted on the harder materials. It can be seen that the lighter the load and the harder the piece, the greater the percentage of error and, therefore, the difference that the authors have obtained between their table and that of the ASM is very close for all practical purposes when all points are taken into consideration.

J. J. KANTER:[6] The statement is made in Mr. Scott's paper that Vickers number is independent of the load. We must not take this conclusion too literally for all material, although it is a good approximation for hard steels, which have reached the limit of their hardening capacity. If a test be made on soft annealed copper, one finds that the variation of hardness of the Vickers number is considerable, particularly at the smaller loads.

If a series of Vickers numbers for annealed metals are plotted against either the load or the diameter of the indentation, one obtains a curve starting to rise rapidly at small loads, attaining a maximum and then falling to a constant number for the larger loads. This sort of curve, of course, is not found unless the metal has a considerable work hardenability. When dealing with work hardenable metals, it can readily be seen that difficulties arise in attempting to make conversion tables to relate one type of test to another where a relatively different amount of work hardening is involved. If we plot Vickers numbers against load or diameter for copper having various degrees of cold working, one finds the greater the degree of cold work, the smaller the load necessary to establish constant Vickers numbers.

We therefore may anticipate greater difficulties in making conversion tables for the working hardenable materials than the authors have had to cope with in their present treatment of hardened steels.

Authors' Reply

Some of the interesting points brought out in the several comments on this paper deserve further consideration. One is Mr. Lysaght's impression that we consider the diamond pyramid hardness scale to be ideal. Such is not the case, our view being simply that the diamond pyramid test approaches more closely to the ideal than any other standard test. Undoubtedly there is distortion of the impression producing abnormality in the hardness scale based on this test both at high and at low hardness values. At the round table discussion on "The Nature of Hardness," Mr. Swanger described a form of indenter that may offer a means for avoiding this abnormality.

Mr. Lysaght's explanation of the discrepancy between the observed diamond pyramid hardness values and those calculated from Rockwell impression depths

[6]Research metallurgist, Crane Co., Chicago.

corrected for elastic recovery is quite acceptable to us. With regard to reproducibility of the diamond pyramid test, we have made comparisons between three machines in our East Pittsburgh Works and found prior to adjustment for correction that they check within a range of ± 15 points at about 800 DPH.

Mr. Sadtler calls attention to the surprising discrepancies in current conversion relations. We can understand them only as a result of double conversion. Suppose, for example, that diamond pyramid hardness is compared with Brinell hardness values obtained with a standard ball, in one case, and Rockwell hardness with Brinell hardness measured with a Hultgren ball. Since these two Brinell balls give widely different values at the same high hardness, there would be a large error in the relation between the diamond pyramid and Rockwell hardness compared through the Brinell values so observed. Nevertheless no published conversion table specifies the type or hardness of the Brinell ball used.

We are glad to have Mr. Sadtler's careful observations for comparison with our own even though there is considerable discrepancy. He finds 853 DPH on 18-4-1 high speed steel at 65 RC while we find 795. This difference is too large to ignore and emphasizes the difficulty of obtaining agreement between laboratories. Intercomparisons are obviously necessary to isolate the cause of discrepancy.

Mr. Sadtler reports also a difference in the Rockwell value on carbon steel from that on high speed steel, both at 853 DPH, namely 66.5 and 65.0 respectively. We have observed the same effect, though not quite so pronounced, since presenting this paper. It is found, however, only in large sections of carbon tool steel in which there is a hardened shell underlaid by a soft core of considerable area. Under these circumstances the shell is under very high compressional stress which undoubtedly accounts for the difference. We find at 895 DPH a Rockwell value ½ to 1 point higher than the conversion value of 68.2. This is one more factor for addition to the list of those which must be considered in the establishment and use of hardness conversion relations.

Mr. Fishbeck and others do not agree with us that there is an exact and reproducible relation between Rockwell and diamond pyramid hardness. We have shown, however, that consistent relations can be obtained if attention is paid to all of the possible sources of variation and error. Mr. Fishbeck mentions surface finish and mass of the test piece. Certainly finish is an important factor, but we have no indication that size is important in these tests, except as mentioned in connection with carbon steel. In the scleroscope test, however, size is a very important factor.

It is very gratifying to have brought out the information which Mr. Kanter presented. While it is beyond the range of our present experience, we expect, nevertheless, to investigate softer metals and to profit by Mr. Kanter's observations as well as those of the other contributors to the discussion of our paper.

A METHOD FOR THE PREPARATION OF METALLOGRAPHIC SPECIMENS*

By George A. Ellinger and Joseph S. Acken

Abstract

A lapping method for the preparation of metallographic specimens has been successfully used at the National Bureau of Standards for several years. Intermediate preparation of specimens is done on a grooved lead-tin (50-50) disk in which emery has been embedded. V-shaped grooves arranged in a rectangular pattern serve to hold lubricants and to catch particles of dislodged emery. Soft metals and those containing nonmetallic inclusions, which are ordinarily considered difficult to prepare, have been polished using this method. Photographs of structures of lead, tin, silver, graphite flakes in cast irons and nonmetallic inclusions and other structural features in steels are shown as examples of the use of this technique.

FROM time to time, in metallurgical literature there have appeared new methods for the preparation of metallic surfaces for microscopic examination. It is significant to note that seldom has there been an important advance in the science of metallography without a corresponding advance in the methods of preparation of specimens. In early days when polishing was extremely crude, according to present-day standards, it was possible to reveal, by etching, only the gross features of structure. As the technique of polishing was improved to reveal finer and finer details, it became possible with modern methods to procure sharp details in specimens magnified several thousand times. The marked advances in recent years, in clarity of detail of metallographic structures presented in present-day metallurgical literature, are believed to be due more to improvements in the preparation of the surfaces than to the improved optical equipment available today.

Although their characteristics are not well understood, consider-

*Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, George A. Ellinger is associate metallurgist and Joseph S. Acken assistant science aide, the National Bureau of Standards, U. S. Department of Commerce, Washington, D. C. Manuscript received June 23, 1938.

able importance is attached to the surface films on polished metals. It is impossible to reveal fine details of the metal structure when they are obliterated by a film of flowed metal at the surface. At the same time it is practically impossible to polish a specimen without causing some surface flow. The finest details of structure are revealed only when the film produced by polishing is thin enough to be entirely removed by the etching treatment.

Recommended procedures for the preparation of specimens have placed more emphasis upon the final polishing and not enough importance has been attached to proper manipulation in the intermediate stages. It is evident that deep scoring or disturbance of underlying metal is fatal to good results, regardless of the excellence of the final polishing.

In general, the intermediate stages of preparation may be accomplished by either fixed or loose abrasives, the first being represented by emery or carborundum papers, and the second by abrasive powders applied with water or other liquids on a cloth of suitable material and preparation.

Deep scratches and severe local distortion below the surface are caused by nonuniform particle size of fixed abrasive on the papers. The same effects may be caused also by grains of abrasive becoming detached from the backing and rolling under the specimen. Scratches and distortion are particularly detrimental to the proper preparation of soft metals such as lead, tin, pure iron, etc.

Loose abrasives applied to a cloth with water or other liquids present the same difficulties, together with the probability of tearing out nonmetallic inclusions in steels and graphite flakes in gray cast irons.

Several years ago considerable difficulty was encountered in the metallurgical laboratories of the National Bureau of Standards in polishing specimens of a certain steel which was very soft and contained numerous inclusions. Loose abrasives tore out practically all of the inclusions. Preparation of the specimens with papers permitted the retention of inclusions, but nonuniform particles of abrasive disturbed the underlying metal so severely that sharp details were not observed after etching. Prolonged final polishing to remove the disturbed metal resulted in the loss of inclusions.

The use of abrasives embedded in a soft lapping block was considered. Pitch laps such as those used in the polishing of optical glass were not satisfactory because of uneven wear. At the suggestion of

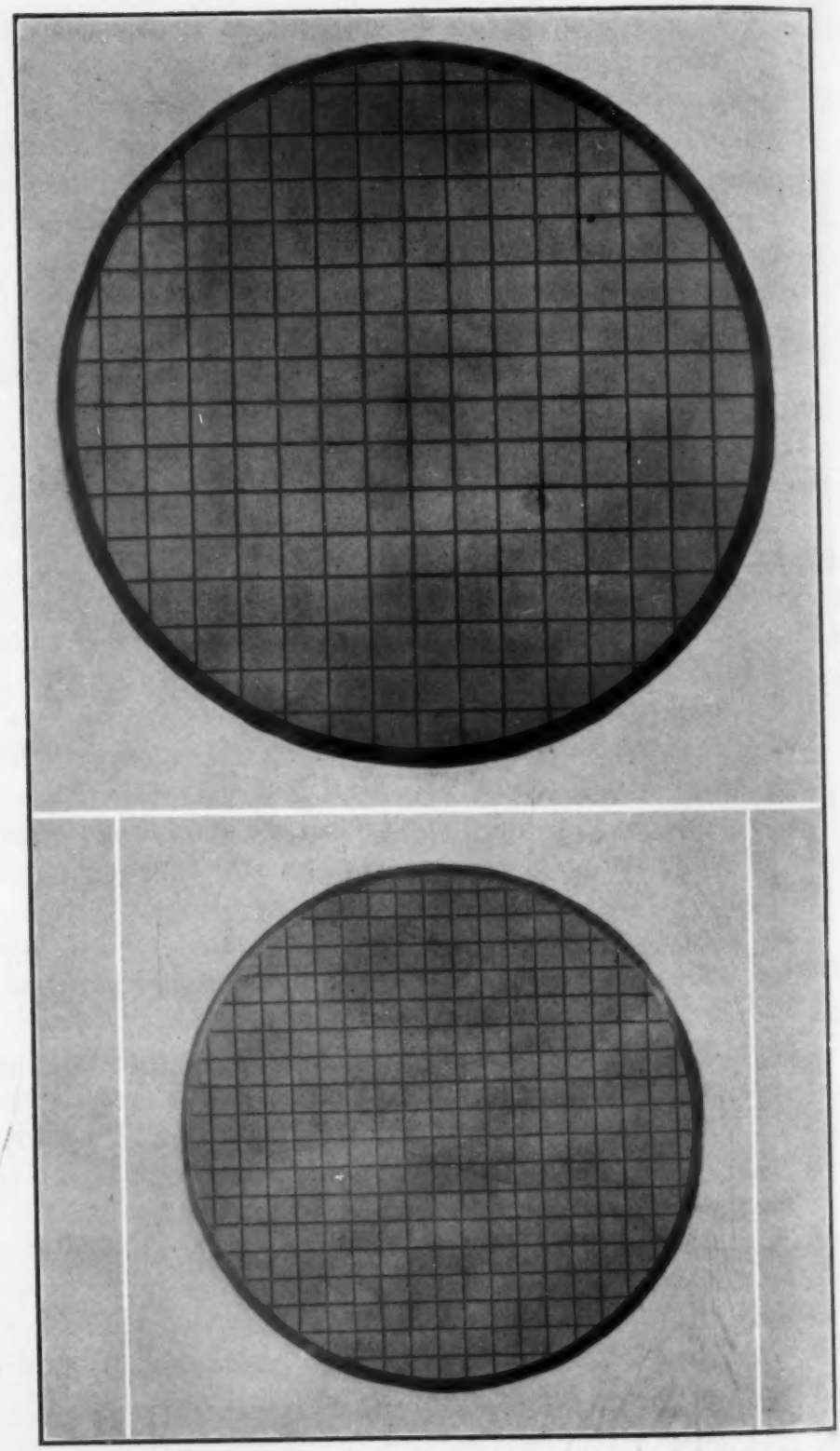


Fig. 1—Lapping Disks for the Preparation of Metallographic Specimens. The Large Disk is a High Strength Cast Iron, the Small One, an Alloy of 50 Per Cent Lead—50 Per Cent Tin.

the optical shop[1] a lapping disk of lead-tin (50-50) alloy charged with an abrasive of suitable size was tried. This procedure proved to be very satisfactory for the particular steel that caused difficulty, a soft steel with numerous inclusions. It has proved to be so useful in the preparation of other metals which are considered difficult to prepare, that a detailed description of the procedure was considered to be a useful contribution to the science of metallography. This paper treats only of the intermediate stages of preparation and does not discuss the final polishing.

Description of Method

The preparation of metallographic specimens on lapping disks is not new. A distinctive feature of the present method is the use of two disks containing V-shaped grooves arranged in a rectangular pattern. These are shown in Fig. 1. The larger disk is a high-strength gray cast iron with the graphite uniformly distributed in very small flakes. This disk is 8 inches in diameter and contains grooves ½ inch apart, milled to a depth of $\frac{1}{32}$ inch, with a 60-degree (included angle) milling cutter. Before milling, the surface was carefully ground on a precision surface grinder. The maximum deviation from a true plane was less than 0.0001 inch over the entire surface. The smaller disk is a lead-tin (50-50) alloy. It is 6 inches in diameter and contains grooves ¼ inch apart, milled to a depth of $\frac{1}{32}$ inch, with a 60-degree (included angle) milling cutter. The surface of this disk was faced flat in a lathe before milling.

The specimens are prepared only on the lead-tin disk, the iron disk being used solely for charging the lead-tin disk with emery and to keep it flat. Charging is accomplished by placing emery of the proper grade mixed with water on the face of the cast iron disk and rotating the lead-tin disk, face down, upon it for about 30 seconds. Emery particles are thus embedded uniformly in the lead-tin disk and it is ready for use. The emery which has not been embedded in the lead-tin disk is brushed off vigorously with a small, stiff hand brush under a generous supply of running water. It is quite important that this excess emery be carefully removed to prevent embedding it in specimens of soft metals.

The use of the lead-tin disk in the preparation of specimens has

[1]Acknowledgment is made to E. A. Webb of the optical shop of the National Bureau of Standards for his assistance and co-operation in the preparation of the laps.

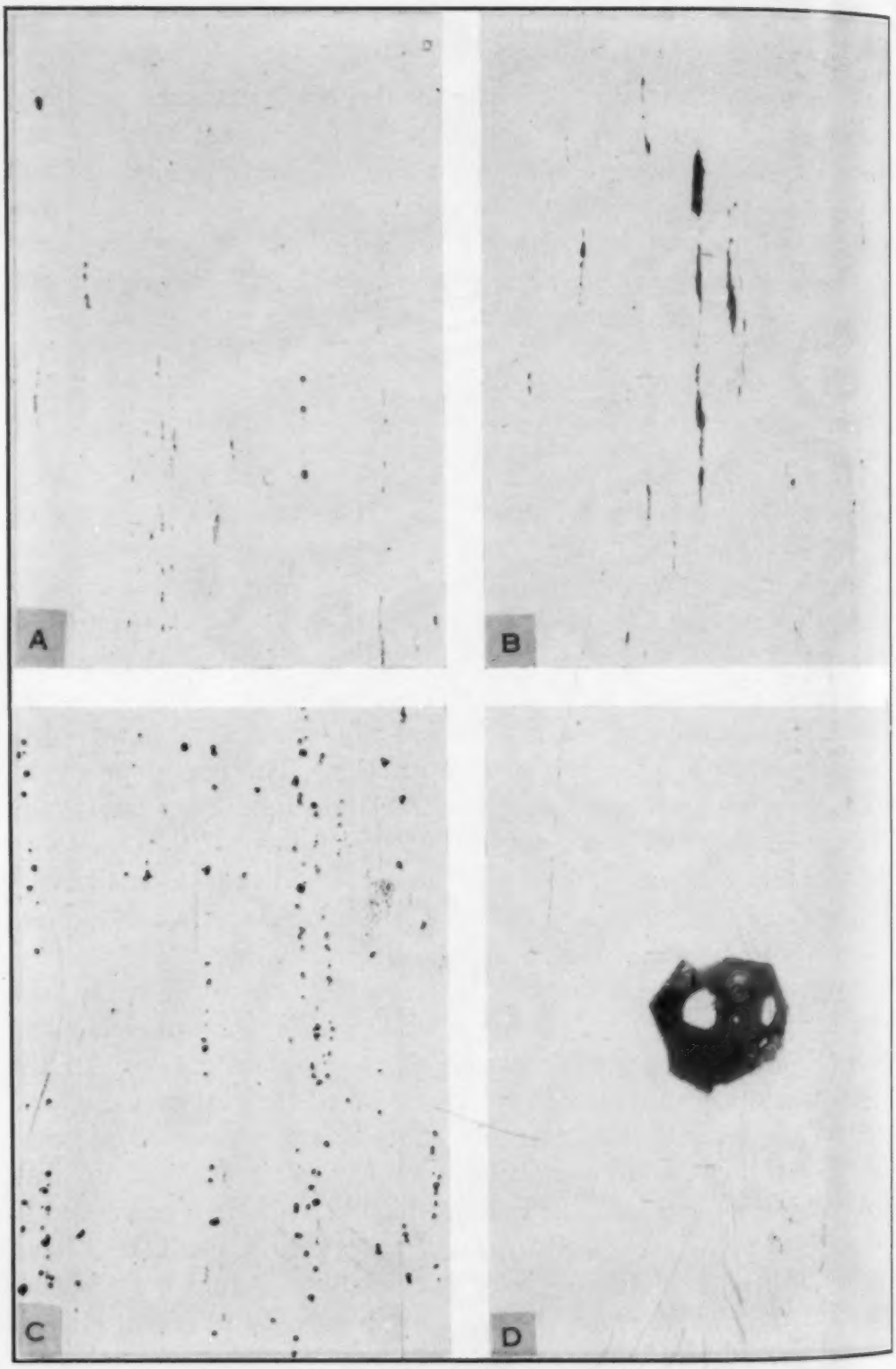


Fig. 2A—Inclusions in a Low Carbon Silicon-Manganese Steel. Unetched. × 100.
Fig. 2B—Inclusions in Low Carbon Manganese-Molybdenum Steel. Unetched. × 100.
Fig. 2C—Inclusions in Low Carbon Copper-Nickel-Molybdenum Steel. Unetched. × 100.
Fig. 2D—Inclusions in Low Carbon 1 Per Cent Aluminum Steel. Unetched. × 500.

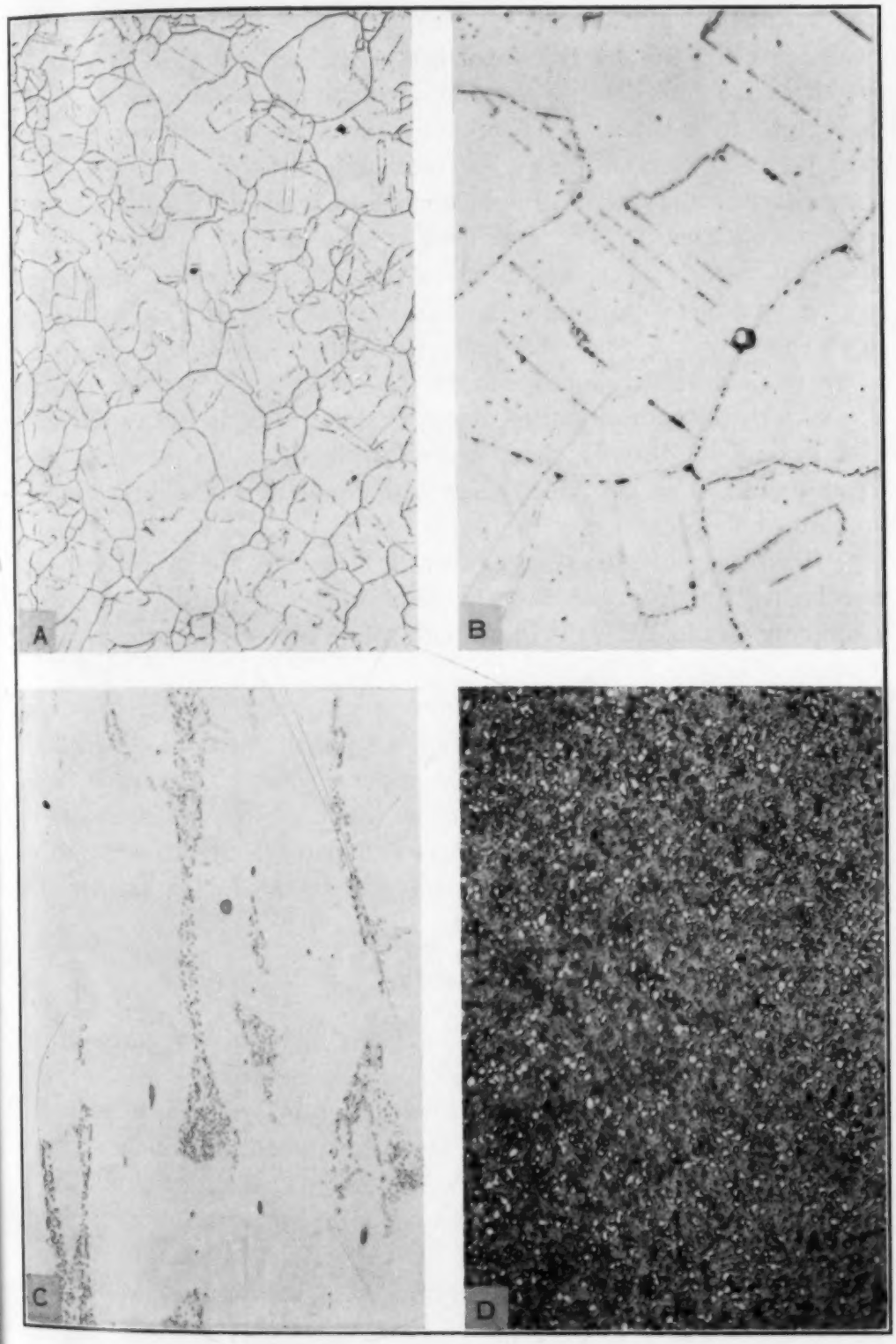


Fig. 3A—18-8 Type Corrosion Resisting Steel. Annealed 6 Days at 750 Degrees Cent. (1380 Degrees Fahr.). Etchant 10 Per Cent Oxalic Acid, Electrolytic. × 100.
Fig. 3B—Same as A. × 750.
Fig. 3C—Annealed Low Carbon Steel Tubing. Etchant 4 Per Cent Picric Acid. × 500.
Fig. 3D—Safety Razor Blade. Etchant 4 Per Cent Picric Acid. × 500.

several distinct advantages. A means of using a fixed abrasive, with water or other suitable liquid for lubrication, is provided. The emery particles are embedded in the disk in much the same manner as they are glued to a paper. The milled grooves serve both for retaining water for lubrication of the surface and as a place of deposit for particles of emery which might become dislodged. Dislodged particles are carried by the specimen to the nearest groove and are dropped, which prevents their further rolling under the surface of the specimen. Ungrooved disks soon become dry and allow the loose abrasive to roll. Of many abrasives tried, emery was the only one which produced satisfactory results. Sharper abrasives such as carborundum caused deep scratches which were quite difficult to remove. Emery, being quite friable, probably breaks up more readily into finer particles, when dislodged, thus avoiding the formation of deep scratches.

Two sets of disks are generally used in the preparation of specimens, one for use with a medium emery (American Optical Company Grade 302), the other with a fine emery (American Optical Company Grade 303½).

The use of the disks produces specimens of extreme flatness, which require considerably less time to polish than those which are rounded or uneven. For example, a specimen of annealed 0.45 per cent carbon steel, ⅝ inch in diameter, was filed flat and processed on two laps ready for final polishing, in three or four minutes, with a surface which did not deviate more than 0.00002 inch from a true plane.

Results

Photographs of specimens of various materials prepared by the lapping method are shown in Figs. 2 to 9, inclusive.

Fig. 2 shows photographs of various types of inclusions found in several "dirty" steels. Fig. 2D is an unidentified inclusion, not elongated by hot working, that was found in a steel containing 1 per cent aluminum. The inclusion was not pitted or torn out in preparation of the specimens.

Figs. 3A and B are photographs of a corrosion-resisting steel of the 18-8 type. This specimen was annealed for 6 days at 750 degrees Cent. (1380 degrees Fahr.). A duplex type of grain boundary structure is shown in Fig. 3B. Fig. 3C shows pearlite completely spheroidized in a matrix of ferrite. Fig. 3D shows the structure of

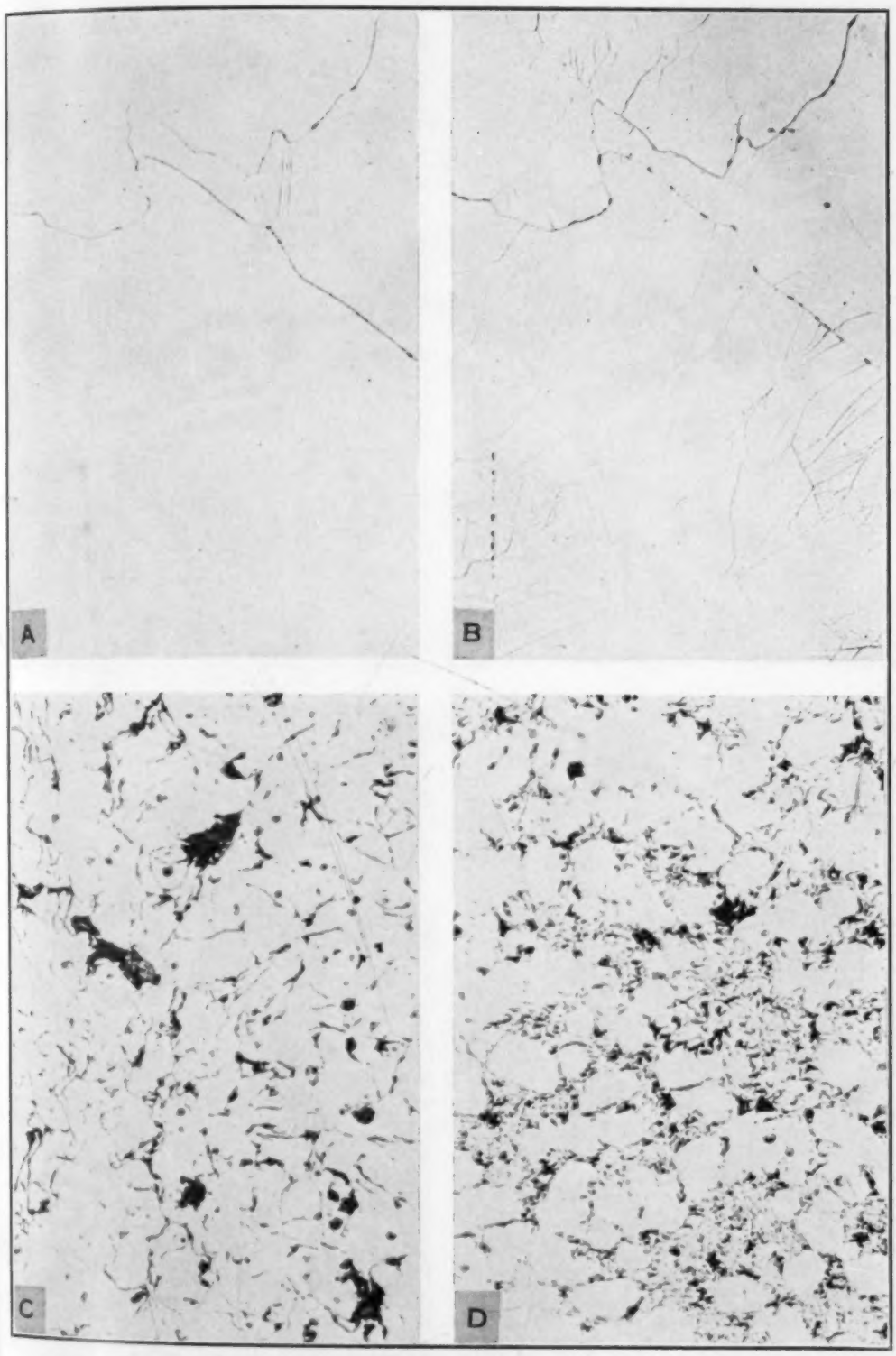


Fig. 4A—High Purity Iron. Etchant 1 Per Cent Nital. × 100.
Fig. 4B—Same as 4A. Etchant 4 Per Cent Picric Acid. × 100.
Fig. 4C—Cast Iron. Unetched. × 100.
Fig. 4D—Cast Iron. Unetched. × 100.

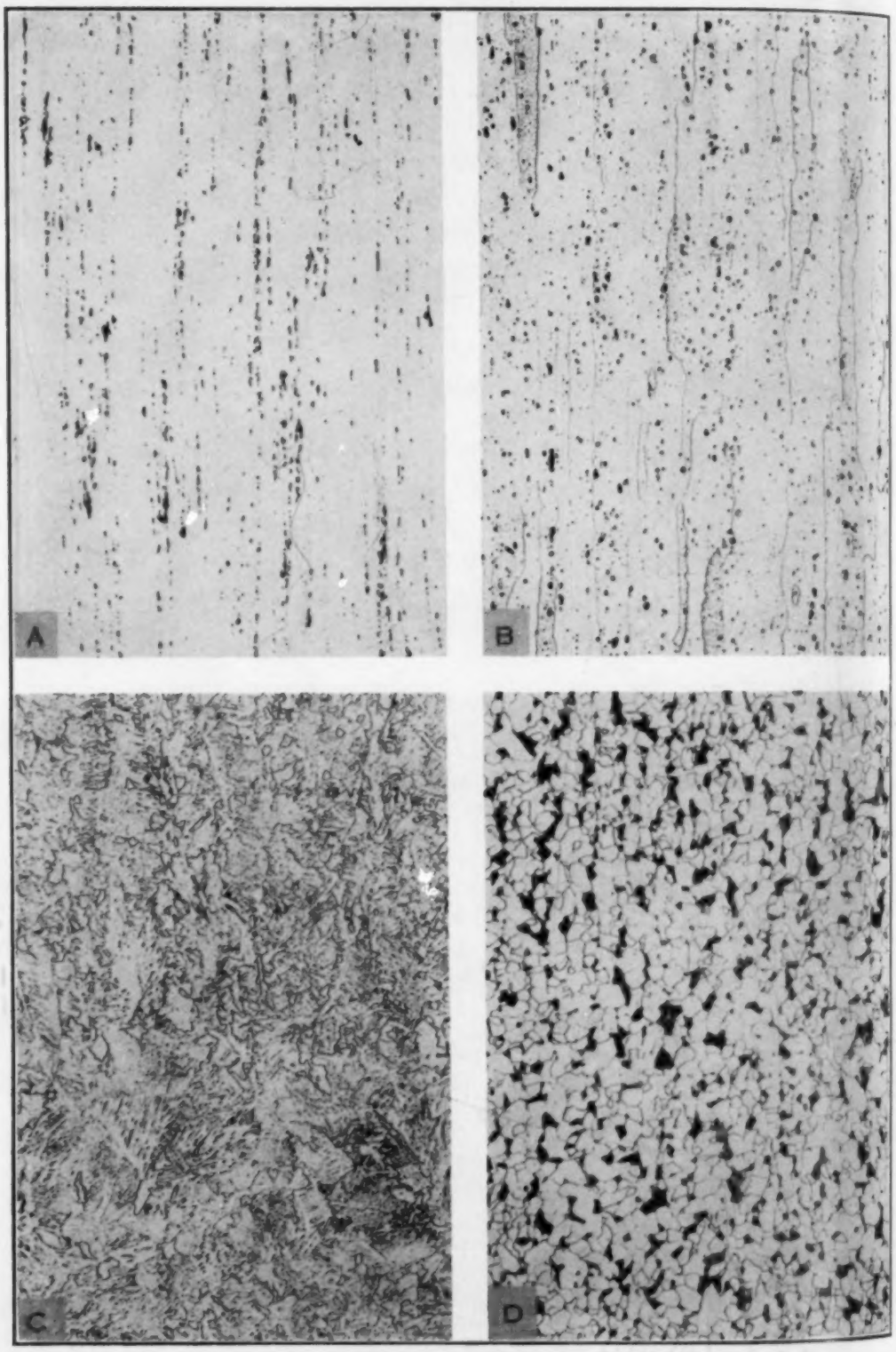


Fig. 5A—Commercial Aluminum, Rolled. Etchant: 1 Part HF, 1 Part HCl, 3 Parts Glycerine. × 100.

Fig. 5B—Aluminum-Copper-Silicon-Manganese Alloy, Rolled. Etchant: Keller's Reagent. × 100.

Fig. 5C—Low Carbon Steel Weld Metal. Etchant: 1 Per Cent Nital. × 100.

Fig. 5D—Rolled Manganese-Molybdenum Alloy Steel Containing 0.10 Per Cent Carbon and 0.45 Per Cent Molybdenum. Etchant 1 Per Cent Nital. × 100.

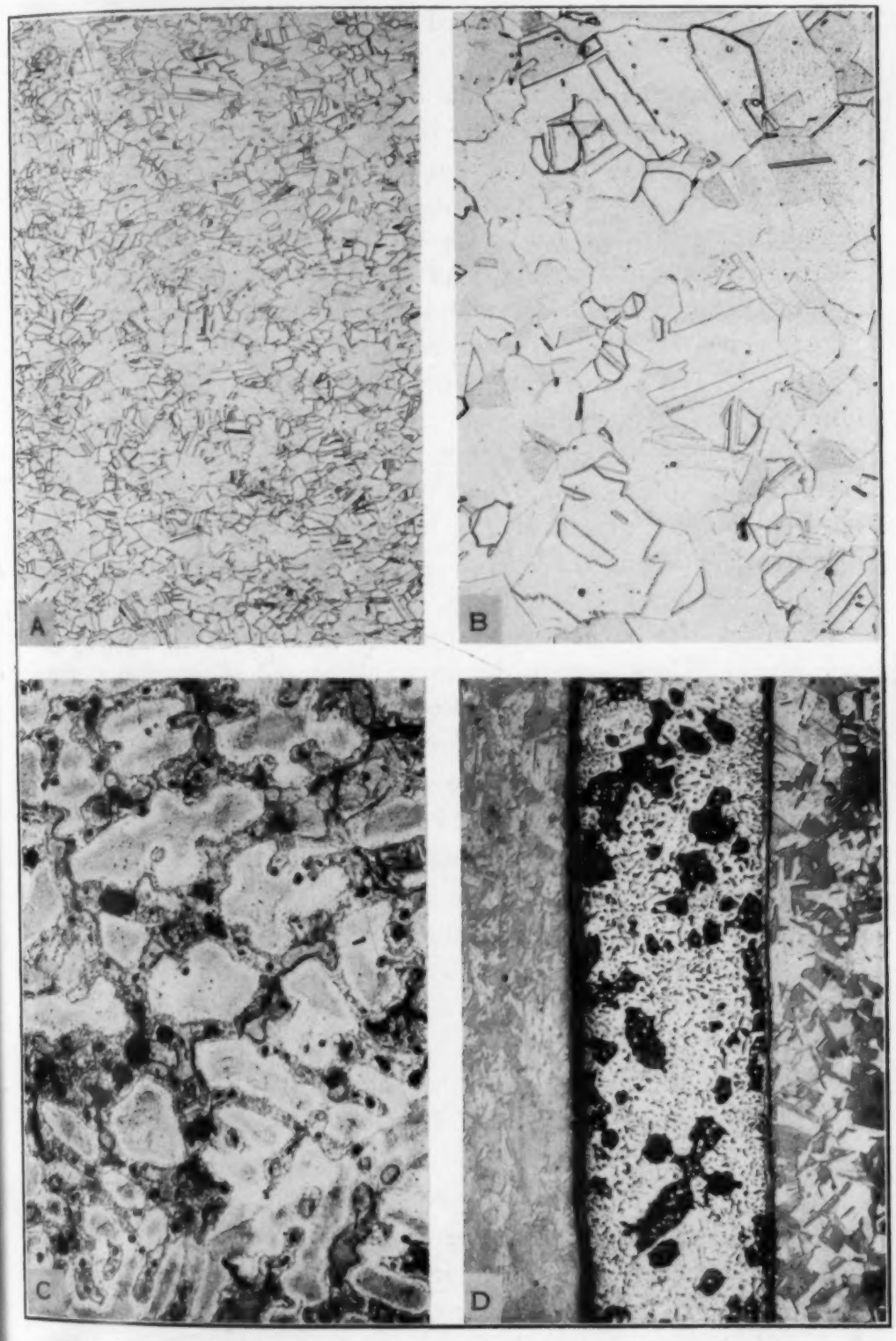


Fig. 6A—Annealed Yellow Brass Tubing Containing 1.25 Per Cent Aluminum. Etchant 10 Per Cent Ammonium Persulphate, Electrolytic. × 100.
Fig. 6B—Yellow Brass. Rockwell Hardness B 9. Etchant same as Fig. 6A. × 100.
Fig. 6C—Cast Red Brass, 85-5-5-5 Type. Etchant same as Fig. 6A. × 100.
Fig. 6D—Two Copper Tubes Soldered. $NH_4OH + H_2O_2$. × 250.

spheroidized cementite in a hard matrix as found in razor-blade steel.

Figs. 4A and B are the same location in an iron of high purity, prepared at this Bureau. Fig. 4B, etched with 4 per cent picric acid in alcohol, shows, in addition to the grain boundaries, an alpha veining pattern. This pattern was not revealed by etching in 1 per cent nital, Fig. 4A. High purity iron is very difficult to polish because of its extreme sensitivity to surface flow and its capacity for work hardening. Figs. 4C and D are of cast irons, showing an almost perfect retention of graphite flakes.

Fig. 5A is a photograph of commercial aluminum and 5B of an aluminum-copper-silicon-manganese alloy. The inclusions and small particles of metallic constituents were perfectly retained in these specimens. Fig. 5C shows the structure of a low carbon arc weld and Fig. 5D the structure of a hot-rolled manganese-molybdenum alloy steel containing 0.10 per cent of carbon and 0.45 per cent of molybdenum.

Fig. 6A shows the structure of an annealed yellow brass tube containing 1.25 per cent of aluminum. Fig. 6B shows the structure of a very soft yellow brass, (hardness—Rockwell B9). These specimens are offered as examples of results on soft brasses of small and large grain sizes. Fig. 6C shows the structure found in a cast red brass of the 85-5-5-5 type, while Fig. 6D shows a joint between two pieces of copper tubing soldered with lead-tin solder (50-50).

Fig. 7A shows the structure of an annealed silver, (99.995 per cent Ag), Fig. 7B, a cast silver-silicon alloy containing 0.03 per cent of silicon, and Fig. 7C, a hot-rolled rod of a silver-silicon alloy containing 1.25 per cent of silicon. Fig. 7D shows the structure of cast tin (99.5 per cent Sn).

Figs. 8A, B, and C show the structure of commercially pure lead; Fig. 8A an electrolytically deposited lead, Fig. 8B commercial lead, and Fig. 8C an annealed cast lead. Fig. 8D shows the structure of "star" antimony containing some lead.

Fig. 9A shows the structure of a lead-coated steel wire. The dark area adjacent to the steel originally contained a zinc bonding layer, which was removed by the etching reagent. Fig. 9B shows a weathered hot-dipped zinc coating on steel wire and Fig. 9C a plated zinc coating on steel wire. Fig. 9D shows the structure of cast pure zinc of the quality used for melting point determinations.

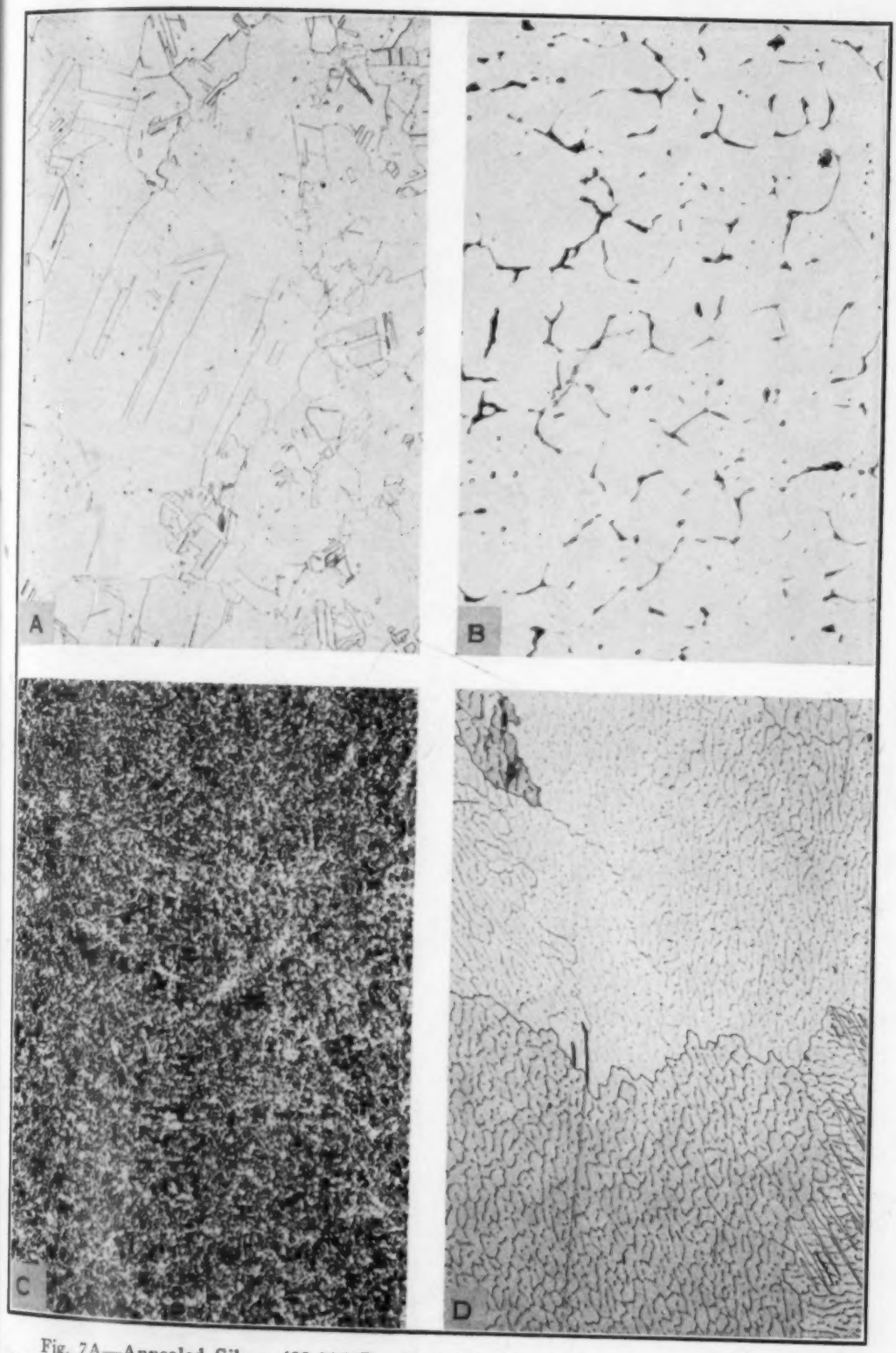


Fig. 7A—Annealed Silver (99.995 Per Cent Silver). Etchant 10 Per Cent Citric Acid, 1 Per Cent Nitric Acid, 89 Per Cent Water, Electrolytic. × 100.
Fig. 7B—Cast Silver-Silicon Alloy. Etchant Citric Acid, Nitric Acid. × 100.
Fig. 7C—Rolled Silver-Silicon Alloy (1.25 Per Cent Silicon). Etchant same as above.
Fig. 7D—Cast 99.5 Per Cent Tin. 10 Per Cent Ammonium Persulphate, × 100.

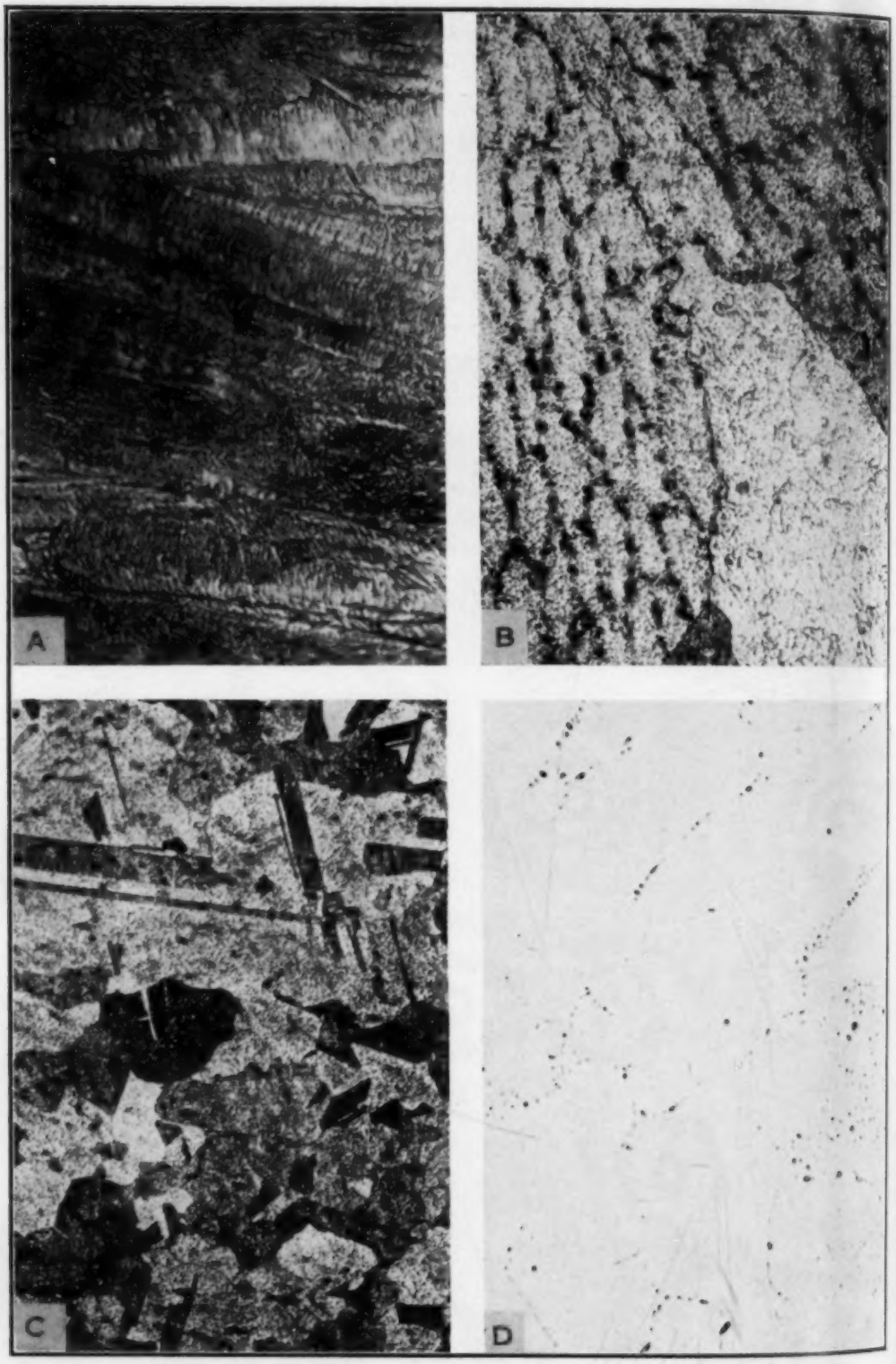


Fig. 8A—Electrolytically Deposited Lead. Etchant 10 Per Cent Perchloric Acid, Electrolytic. × 500.
Fig. 8B—Cast Lead. Etchant 10 Per Cent Perchloric Acid, Electrolytic × 100.
Fig. 8C—Annealed Lead. Etchant 10 Per Cent Perchloric Acid, Electrolytic. × 100.
Fig. 8D—"Star" Antimony, Containing Lead. Unetched. × 100.

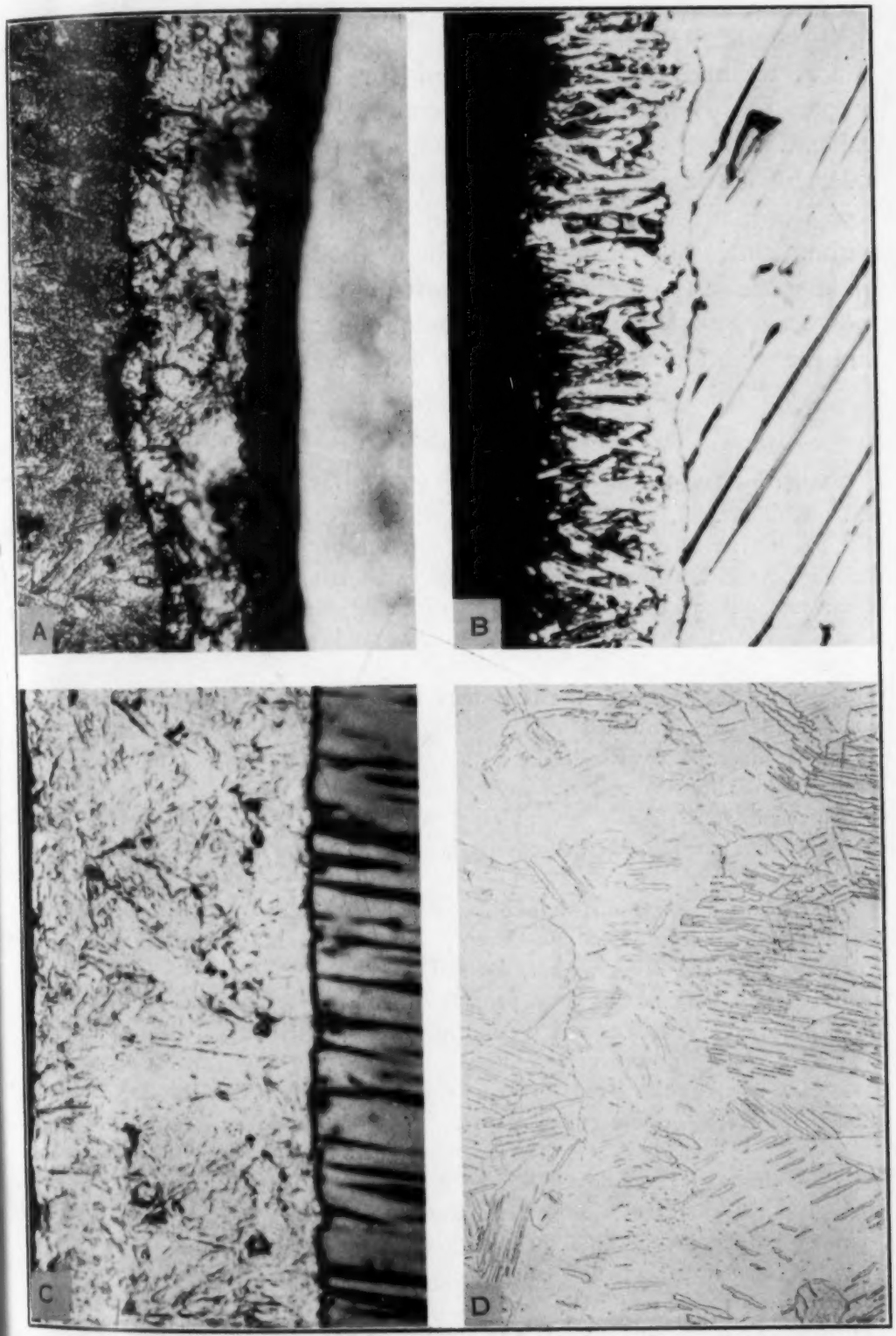


Fig. 9A—Lead Coating on Steel Wire. Etchant 10 Per Cent Perchloric Acid, Electrolytic. × 250.
Fig. 9B—Hot Dip Zinc on Steel Wire. Weathered, Palmerton Reagent. × 500.
Fig. 9C—Electrolytic Zinc Coating on Steel Wire. Etchant, Palmerton Reagent. × 500.
Fig. 9D—Cast Zinc, Melting Point Quality. Etchant, Palmerton Reagent. × 100.

Conclusions

A method has been described for the intermediate stages of preparation of metallographic specimens which has proved to be of value. The method is rapid, efficient, and provides specimens of considerable flatness for the finishing stage. Specimens are remarkably free from surface distortion, and inclusions of all types are retained without pitting or tearing out. The method has been found to be of great value in the preparation of soft metals, which are quite difficult to process by other methods. The equipment required is inexpensive and the technique is not difficult to acquire.

DISCUSSION

Written Discussion: By C. W. Mason, professor, chemical microscopy and metallography, Cornell University, Ithaca, N. Y.

The writer is convinced that the most serious relief polishing, removal of inclusions, and rounding of edges occur in metallographic preparation by the usual methods at the first stage of surfacing on cloth laps, especially if a relatively coarse abrasive ("600-mesh" carborundum or alundum, for example) is used. This can be plainly observed with cast irons, in which graphite, perfectly retained through the last stage with the emery papers, is rapidly torn out and the voids rounded by the severe cutting action of the first lap, even though it may be covered with a thin hard cloth or even with wax. Very cautious procedure is essential at this stage, and if the retention of inclusions is a problem it is usually desirable to pass directly from the last paper to the levigated alumina lap, even though it is slower in removing the scratches from the paper.

Any procedure, such as that contributed by the authors, which will minimize the above difficulties is most welcome. One might wish that they had made more study of the disks with embedded emery, for the way the particles are anchored and the amount they project are of great importance in governing the depth of the scratches and the cutting action. It is a fact that an abrasive, used on a cloth lap, can give a surface on steel which is adequate for studies at × 500, whereas the same abrasive on a bronze lap yields scratches far worse than those from the last emery paper.

Obviously the fineness of the microscopic or submicroscopic scratches that make up the surface of any specimen that has been prepared by true abrasion rather than by surface flow is determined not directly by the diameter of the particles but by how deeply their corners and edges score the sample. They may be likened to cutting tools lightly held at random, and under chance pressures, as contrasted with tools of the same size, used with a heavy feed.

Embedding in soft metal laps, under precise control, will permit more systematic results, but other indirect factors, such as viscosity and surface tension of the suspending medium for instance, may be of primary importance in the more usual methods. Until we have some rational analysis of the micro-

scopical and submicroscopical aspects of surface abrasion, and have learned how to control certain of the variables that are now left to chance, even apparently specific directions cannot always yield consistent results for various workers.

It is generally considered that emery, although less hard, is tougher than carborundum, and in many grinding operations the latter is, because of its friability, so rapidly reduced as to decrease its cutting action severely. (This is one of the main reasons why emery is used in preference to carborundum for grinding glass).

The illustrations of cast irons in particular are at too low a magnification to show how well the graphite has been retained and the edges of the matrix kept sharp. Similar criticism might be made of other preparations.

Written Discussion: By Fred M. Arnold, metallurgist, Kobe, Inc., Huntington Park, California.

For the past four years we have been conducting an extensive program of testing a considerable number of alloys for their resistance to wear. Our method of preparing the test pieces, conducting the wear tests, and measuring the wear with some of the results obtained, was the subject of a paper entitled "Frictional Wear of Lubricated Surfaces," published in TRANSACTIONS, American Society for Metals, Vol. 26, 1938.

The method worked out for preparing the wear test blocks is based on lapping them in a manner similar to the method described by Messrs. Ellinger and Acken in this paper.

Practically all our samples were hard wear resisting alloys. To prepare the test blocks it was necessary to lap them to within about half a wave length of being optically flat and to obtain a good polish. This was to produce a surface which could be reproduced on every new test block and one on which the slight amount of wear occurring in twenty-four hours could be measured with an optical test plane.

It was sufficient in our case to use the cast iron lap directly, charging it with lapping compounds and rubbing the test blocks on the surface by hand. Rectangular cast iron blocks 9x12 inches were planed flat and scored every ½ inch with $\frac{1}{16}$x$\frac{1}{16}$ inch grooves in a manner to produce a lap which would function similar to the cast iron lap shown on page 384.

In polishing our hard blocks we go directly from a fine grinding wheel onto a lap charged with 800-grain crystolon. About five to ten minutes are required to free the surface from grinding marks. Benzol is used to promote rapid cutting and very little abrasive is used. After the 800-grain lap a finishing lap lightly charged with 900-grain crystolon is used. A surface flat to within two light bands can be obtained by hand polishing in 20 minutes.

In order to convey some idea of the finishes produced by these steps, we prepared photomicrographs of the surfaces at × 50 magnification. These are shown in Fig. 1. The photomicrograph on the top shows the final finish obtained on a cast iron lap charged with 900-grain crystolon. The center photomicrograph shows the finish obtained with 800-grain crystolon. The lower photomicrograph is obtained by fine grinding with a 36T22 Aloxite cup wheel.

We were also able to obtain profilographs of these surfaces made through the courtesy of W. G. Hildorf of the Timken Roller Bearing Company. These

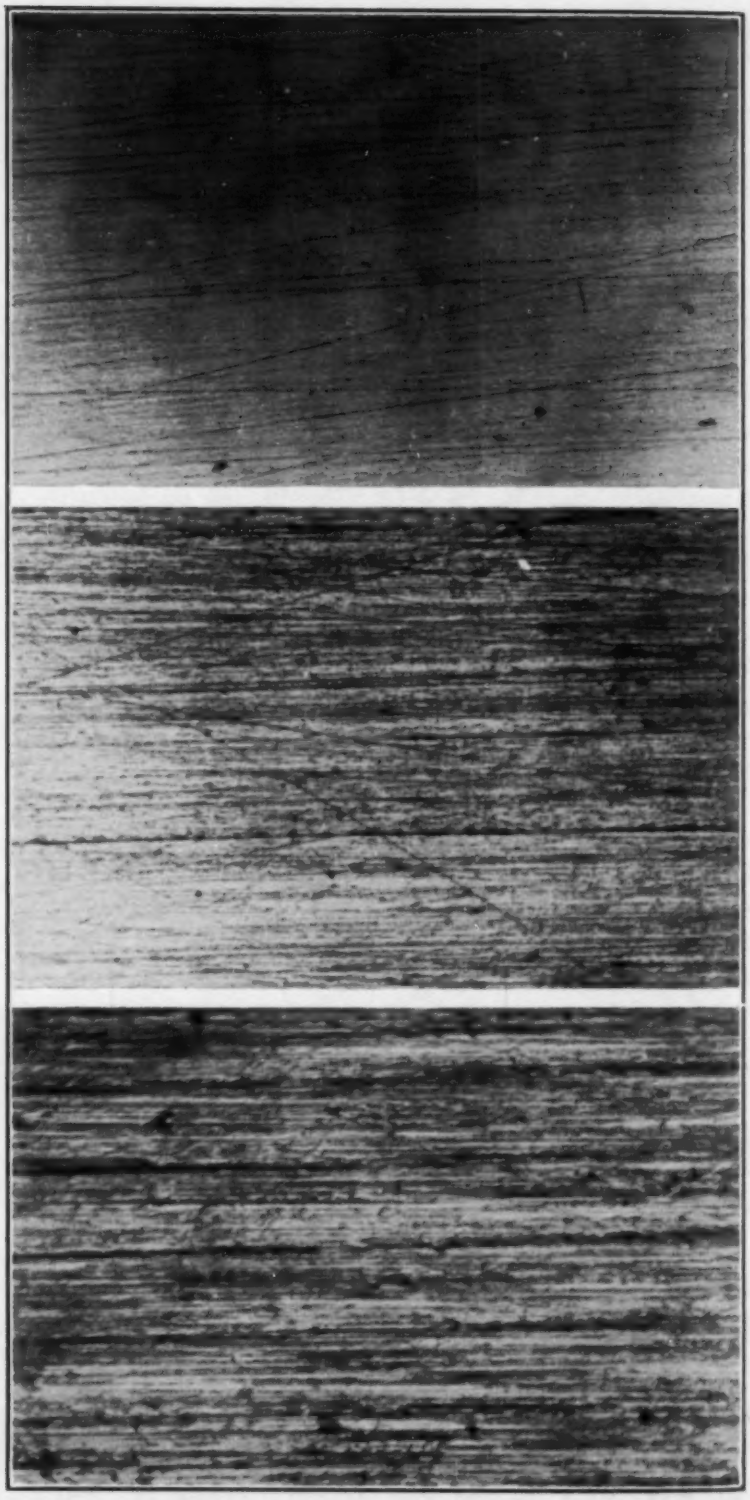


Fig. 1—Micrographs at × 50 of Finishes on Text Blocks. Top, Finish Obtained by Lapping with 900-Grain Crystolon. Center, Semi-Finished Surface Lapped with 800-Grain Crystolon. Bottom, Original Finish as Ground with 36T22 Aloxite Wheel.

are reproduced in Fig. 2. The vertical movement of the tracer point is about 100 times greater than the horizontal displacement. The exact scales are drawn on the traces.

The same three stages of finish are represented as noted beside the traces. This shows very clearly the excellence of the final finish. The bottom trace

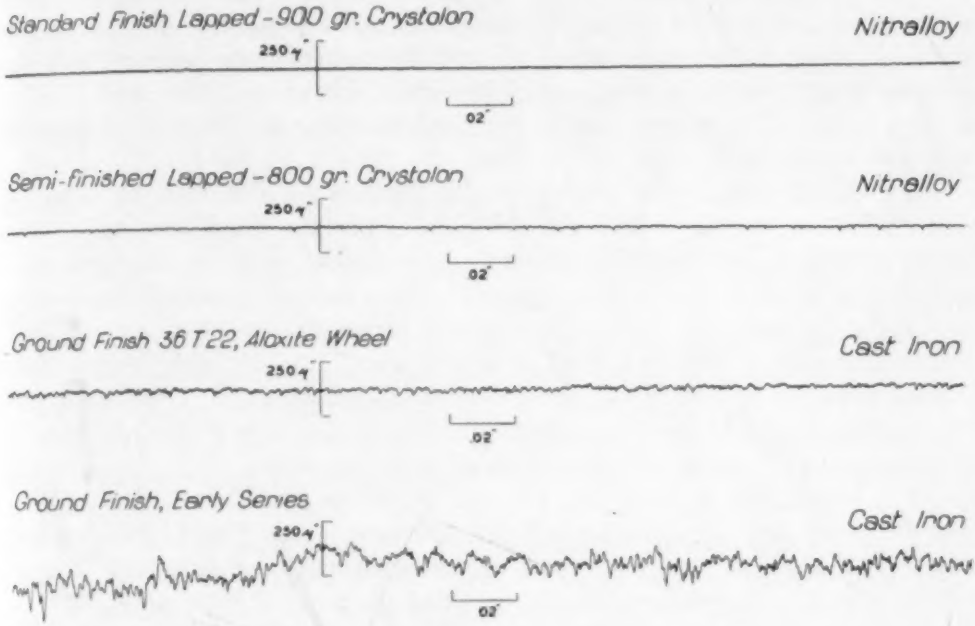


Fig. 2—Profilographs of Four Types of Surfaces.

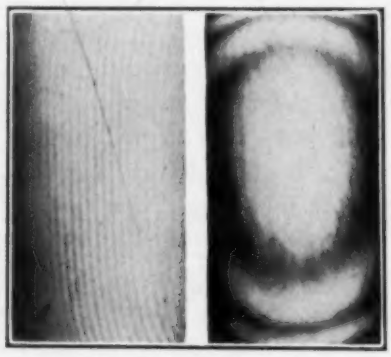


Fig. 3—Lapped Test Block Showing Refraction Patterns. The Pattern on the Left is Due to an Air Film Between the Blocks. At the Right the Test Plane is in Contact with the Test Block.

is the result of less careful grinding. Even this surface can be lapped flat on the two laps in about twenty minutes.

The degree of flatness obtained by this hand lapping method is illustrated by Fig. 3, which shows photographs of refraction fringes, occurring between the polished surface and an optical test plane under a mercury vapor light.

These intermediate polishing steps are so rapid, and leave hard specimens

in such excellent condition for final polishing, that it becomes a great time saver and metallographers will appreciate Mr. Ellinger's and Mr. Acken's efforts and their consideration in bringing the method to our attention.

Written Discussion: By J. W. Freeman and R. Schneidewind, department of engineering research, University of Michigan, Ann Arbor, Mich.

The authors are to be congratulated for presenting an excellent paper describing a new method of preparing metallographic samples. The initial steps generally used in the preparation of metallographic specimens are both time consuming and unsatisfactory, especially when the proper care and technique are not used. A good preparation for final polishing is not only essential for satisfactory results, but also saves time.

We cannot discuss the merits of this method on the basis of experience with it; but we can agree that the principle of using a fixed abrasive is sound. The procedure under discussion seems to have special merit on the basis that it can be applied to so many materials with the excellent results illustrated.

Our experience has shown that bonded abrasives similar to those used by electroplaters have been successful in giving a rapid polish with results similar to those obtained by the authors on graphite in cast iron and inclusions in steel. The success of our method is undoubtedly due to the abrasive being "fixed" in the wax cake built up on the cloth-covered polishing disks.

It is interesting to note that the two polishing procedures mentioned here have been adopted from industrial polishing methods. Fixed abrasives have been found superior to loose powders for industrial polishing and it seems unusual that metallographers have not applied the method more generally.

We have had some experience with the use of diamond laps such as used in polishing commercial and gem stones in the course of work done on hard metals. We had diamonds embedded in a matrix of a metal whose Rockwell C hardness was 82. It was desired to polish this material as well as various tungsten carbide alloys in order to determine the closeness of the bond between stones and metals. Ordinary polishing methods failed due to the presence of the stones. The diamond lap was able to polish both metal and stones in one polishing operation with a finish such that practically scratch-free surface was exposed at 1000 diameters. In polishing these same metals without the stones, considerable difficulty was encountered with the usual methods due to chattering on the grindstone and extremely slow polishing. The diamond lap polished satisfactorily in this case, also.

The lap consisted of a revolving disk of cast iron. No lines were scored on the surfaces. The abrasive was diamond dust mixed with vehicle such as turpentine and was applied by means of the end of a match stick. The diamond powder became embedded in the graphite pores of the cast iron. For softer material it is very likely that carborundum or similar dust could be used in place of the diamond dust.

Written Discussion: By A. B. Wilder, assistant professor of metallurgical engineering, University of Illinois, Urbana, Ill.

The authors of this paper have presented valuable results for those interested in the preparation of specimens. The composition of a lapping disk is a factor of considerable importance and it would be of interest to know the advantages of a lead-tin disk compared to lead or wax.

The metallurgist should have available a satisfactory automatic polishing machine so that this stage of metallurgical practice could be placed upon a sound scientific basis. It would be of interest to have the comments of Messrs. Ellinger and Acken upon the application of their method of polishing to the automatic polishing machine.

The variables in photography should be eliminated as well as those in polishing. It is possible that a satisfactory exposure meter would contribute toward a scientific method for photographing metallurgical specimens. The industrial laboratory as well as the academic laboratory could profit a great deal by improved methods of manipulation.

Oral Discussion

E. G. MAHIN:[2] I suppose that the preparation of metallographic specimens will be discussed to the end of time. It is well known among metallographists that one man can devise details of a method whereby he obtains beautiful results and another man using the same method would not be able to obtain the same results. The human element enters into this very strongly.

I. A. ROHRIG:[3] In the metallography directly connected with the examination of specimens used in steam power-plant work, we often have occasion to examine intergranular cracks. Frequently these are angular voids running at random orientation down through the metallographic aggregates. It is important to preserve all corners and edges to accurately see the path of intergranular cracks. They are very important in steam power-plant work. We find that we can very easily preserve those surfaces by following Mr. Vilella's suggestion of using the emery papers and finally glazing the 000 emery paper with graphite and then going directly to a cloth lap, using alumina.

I would like to ask the gentleman from the National Bureau of Standards if his procedure accurately preserves those voids and, at the same time, affords accurate examination of the phenomena, such as strain lines often accompanying the strained crystals in these cracks.

W. A. SCHUMACHER:[4] I would like to ask the authors if their method is faster than my present method in speed and duplication of results. In the polishing of wire specimens embedded perpendicularly in bakelite, my present method entails the use of a coarse-grained roughing wheel, No. 280 C Trimite alumina oxided paper, No. 400 C Trimite alumina oxided paper, No. 000 emery paper and No. 0000 emery paper in the so-named order. From thence I go to the conventional levigated alumina wheel.

I am wondering whether or not this method of using lead-tin laps will duplicate my results, and if so the number of individual lap steps necessary.

I would also like to know where the lead-tin laps may be purchased.

E. G. MAHIN: How long do you suppose that metallographic polishing will be an art? We like to say that metallurgy is among the oldest of arts but the youngest of sciences. I wonder if the preparation of metallographic specimens is always going to remain an art.

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[2]Professor of metallurgy, University of Notre Dame, Notre Dame, Ind.
[3]Research metallurgist, Detroit Edison Co., Detroit.
[4]Research metallurgist, Wm. D. Gibson Co., Chicago.

Authors' Reply

The authors appreciate the interest shown by those offering discussions of the paper. Obviously, in offering a method which differs somewhat in detail from those generally used, some confusion in application generally arises. There are several points of interest which we wish to cover at this time.

Professor Mahin states that carborundum is more friable than emery and therefore breaks up more readily, losing cutting efficiency rapidly. It may be true that synthetic emery is tougher and not as hard as carborundum but it is our understanding that natural emery is somewhat harder and also more friable than carborundum. Consequently the natural emery is broken up in the lapping process, producing smaller and more uniform scratches than either carborundum or synthetic emery.

It has been impossible, of course, to test all of the abrasives which are obtainable today. Undoubtedly there are others which may be as satisfactory as those which are used in our work.

Water was used as a suspending medium for the abrasive because it was found to be satisfactory and always available. Other inert media such as kerosene and benzol were tried with results practically the same as with water.

The use of the cast iron plate for lapping specimens directly was found to yield unsatisfactory results for metallographic polishing. The surface of the specimen was scoured and contained scratches which were not uniform in depth. For this reason we use the cast iron plates only to charge the lead-tin disks.

In answer to Professor Wilder's question concerning the advantages of the lead-tin disk as compared with lead or wax, we have tried neither. Paraffin disks have been tried with but little success since they are soft and tend to become uneven after the first few passes. Lead-tin is somewhat harder than lead and offers greater resistance to flow, at the same time being soft enough to permit embedding the abrasive.

All of the lapping done at this Bureau has been done by hand, but we can see no reason for not adapting the method for automatic polishing.

In line with Professor Wilder's suggestion that an exposure meter would assist greatly in photographing metallurgical specimens, we have realized for some time that it is extremely difficult to record the relatively small amounts of light reaching the photographic film by means of the meters available. At the present time we are working on the development of such a meter which we hope will be useful in this field.

From experience we can assure Mr. Rohrig that the edges of cracks may be retained with perfect sharpness. In addition we recently have had occasion to study intergranular penetration of steel by molten zinc and have had no difficulty in retaining the zinc at the grain boundaries of the steel.

Mr. Schumacher's method is one similar to some of those which have been used at this Bureau. We believe that we can prepare specimens faster using the laps, but speed is not always the prime requisite. Quality of surface is generally of more importance than speed of polishing.

POSSIBLE USES OF RADIOACTIVE SUBSTANCES IN THE TESTING OF METALS

By Herman F. Kaiser

Abstract

Radioactive substances, in the capacity of indicators, have found much use in several fields of research. This paper represents an attempt to estimate the possibilities and also the limitations in the use of radioactive indicator substances in the detection of defects in metallic materials and parts. Some preliminary experiments in this direction are described.

RADIOACTIVITY has furnished a powerful tool to the research worker in medical and biological fields and by its applications many new lines of research previously thought impossible have been opened up. In the metallurgical field, also, the research worker has benefited to some extent, for example, by the introduction of the gamma ray technique (1) (2)[1] for the inspection of castings, and by the use of radioactive substances in studies (3) (4) on diffusion and transformation processes in certain alloy systems. On the whole, however, the use of radioactive materials has not become as marked in metallurgical research as in biological research because of certain experimental conditions such as the great opacity of metals to radiation and the relative slowness of the kinetic processes in metallic systems as compared to the much more favorable conditions found in organic materials and systems.

In spite of these limitations, radioactive materials should find considerable use in metallurgical research. The use of radioactive substances as indicators has certain unique features that no other conceivable method of indication can have. The indication depends on atomic, or better said, on nuclear properties which are quite independent of temperature, pressure, state of chemical combination,

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[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The author, Herman F. Kaiser, is a member of the staff of the Division of Physical Metallurgy, U. S. Naval Research Laboratory, Washington, D. C. Manuscript received June 24, 1938.

and so forth. Furthermore, the radiations from radioactive atoms include very penetrating kinds of radiation so that their presence can be detected at a distance in places unseen and often inaccessible to physical inspection.

It is not the purpose of this paper to discuss all the uses that have been made of radioactivity in metallurgical research but rather to discuss its possible application in the practical problem of detecting defects in metallic materials and parts. While it is obvious that, given a piece of metal which contains defects on the surface or in the interior, it should be possible to reveal the presence and possibly also the magnitude of these defects if means can be found for introducing radioactive material in sufficient quantity into these defective places. This scheme depends for its success on certain factors which will be discussed at length below. These principal factors are (a) the means employed for introducing radioactive material into the defective localities; (b) the properties and availability of the radioactive material, and (c) the means employed for the detection of this radioactive material once it has been introduced into the metal part.

Review of Factors Involved

Assuming that suitable radioactive substances are available, the factor of prime importance is the technique for introducing this radioactive material into the faulty places in the metal. If our radioactive material is in a gaseous state it will pass by itself into surface openings in the metal piece and if the temperature of the metal is sufficiently high, it may even pass through the channels between the atoms of the crystal lattice by atomic diffusion. In this way it is quite possible, given enough time, to introduce radioactive atoms into any interior cavity or fault in the metal piece. While this is optimistic in principle the fact that diffusion processes are slow and that perhaps even elevated temperatures are required at once puts a serious restriction on the practical application of this quite general method. Thus it is necessary to conclude that for work at ordinary temperatures the method is limited to surface defects or defects that have access to the surface. This, however, is not too discouraging when we remember that many serious defects leading to failure arise at the surface of the metal part.

In the above it was assumed that the radioactive atoms were in a gaseous state. At elevated temperatures this is the stable state

of most substances but at ordinary temperatures only a number of substances are in this condition. Fortunately this class includes some of the natural radioactive elements such as radon and thoron so that it will always be possible to have a gaseous radio element for the purpose in hand.

Gaseous radio elements, however, have short "half lives," that is, decay quickly by transformation into other radio elements so that they are neither abundant nor inexpensive. Furthermore, if proper precautions are not taken they are dangerous materials to use. For these reasons it is necessary to discuss the possibility of substituting radioactive fluids for radioactive gases with the gained advantage of obtaining much higher concentrations of radioactive atoms. Various kinds of solutions of radioactive material can be prepared: (a) aqueous solutions (many of the compounds of the radio elements are fairly soluble in water and the gaseous radio elements dissolve according to Henry's law) and (b) nonaqueous solutions of radioactive compounds or gases.

The solubilities of the radioactive compounds in water are on the whole considerably better than those for organic solvents but water as a solvent has certain features objectionable for the present purpose. Its surface tension limits its penetration into fine pores and cracks. Means to solve this difficulty can perhaps be found. Secondly, metals in general have a tendency to react electrochemcally with water giving objectionable corrosion or plating effects which can be avoided by using a testing fluid which does not react with the metal.

While the solubilities of the inorganic radioactive compounds in organic solvents are not good there is reason to hope that organic fluids containing fairly good concentrations of radioactive substances can be produced by the organic chemist. The introduction of lead into gasolene illustrates what may be done with metallo-organic compounds. Oils, especially light oils of the "penetrating" type, would seem to be desirable carriers of radioactive material.

Finally in this discussion on the technique of introducing radioactive material there is yet to be mentioned a third possibility. This is the use of viscous fluids in which the radioactive material is held as a mechanical suspension. This type of fluid medium has the disadvantage that it is not free-flowing but it can be made to do so by the application of hydrostatic pressure. This method has a certain advantage over the others mentioned in that a high concentra-

tion of radioactive material may be obtained. The disadvantage that additional external apparatus is required to force such material into the cracks is not serious because hydraulic pressure apparatus of all kinds is in everyday use. Further on in this paper a specific example will be given of such a technique.

Having discussed the various possible means whereby radio elements may be introduced into the defects in a metal part, the next topic to be discussed is the availability and suitability of the radio elements for this purpose.

At the present time there are known to be about forty natural radioactive elements including rubidium and potassium which two are weakly radioactive. Excepting the last two, the radio elements are genetically related so that they may be grouped into three series called the uranium, actinium, and thorium series. In each of these the radio elements are formed by successive transformations from a parent substance. These substances are two isotopes of uranium and the element thorium.

During the past few years research in radioactivity and nuclear physics has shown (5) that practically all of the stable elements can be made artificially radioactive by bombardment with ions accelerated to great velocities in supervoltage (1 to 8 million volts) discharge tubes or in the magnetic cyclotron. In the process of collision of an ion with a stable nucleus a radioactive isotope of that nucleus is formed. There are now known to be over 220 radioactive isotopes covering the entire periodic table and some new isotopes with atomic numbers between 92 and 96. These radioactive isotopes have half-lives ranging from a few seconds to several years and can therefore be considered as potentially useful. The cost of producing these artificial radio elements is high at present so they cannot be expected to become commercially available for some time to come. Therefore, in the following only the natural radio elements will be considered as being immediately applicable to the problem under discussion.

The principal and best known radioactive elements are uranium, radium, and thorium, from which, as mentioned above, a number of other radioactive elements are formed by natural radioactive disintegration. Uranium salts are weakly radioactive and serve mainly as sources for preparing radium. Radium salt in pure form is a powerful source of radioactive radiations but even at present it is quite expensive. Thorium, like uranium, is weakly radioactive but

serves as the material for preparation of the powerful mesothorium. Both radium and mesothorium give off gaseous decomposition products known as radon and thoron. The half-life of the former is 3.85 days while that of the latter is only 54 seconds. For this reason only radon has found any commercial application. At present compounds of uranium, radium, thorium, and mesothorium as well as radon can be purchased. The 1937 Minerals Yearbook (6) states the price of sodium uranate as $1.25 per pound; of radium, as $20 to $35 per milligram of radium metal; of thorium nitrate, as $2.20 per pound; of mesothorium, as $35 per milligram of MsTh; and of radon, as $2.50 to $4.00 per millicurie (radon in equilibrium with one milligram of radium).

Table I lists the radioactive elements of the uranium-radium series in their order of disintegration together with their most important radioactive properties. From this table many facts of interest for this work may be derived.

Since thorium is commercially available in quantity at fairly reasonable prices it may be well to see what it has to offer in the way of radioactive properties. A study of Table I shows that a mass of thorium salt old enough to have present and be in equilibrium with all of its decay products will emit several kinds of radiation: α-particles, β-particles (electrons), and γ-rays. The relative intensities of these radiations from the given mass will depend on the amounts present of the elements producing them so that for the present problem it is of importance to estimate, at least, what may be expected. The bulk of the given material is thorium. This gives off only α-particles of 2.58 centimeter range and gives off 4.5×10^3 of these a second per gram. However, a gram of thorium in equilibrium with all of its decay products gives off 2.7×10^4 α-particles a second. (For comparison one gram of radium alone gives off 3.7×10^{10} α-particles and in equilibrium 14.1×10^{10} per second) (10). The amount of mesothorium in equilibrium with one gram of thorium has been found to be about 0.52×10^{-7} grams. The amount of mesothorium produced by one gram of thorium per year is around 3 micrograms per kilogram. In respect to α-particle radiation, however, mesothorium is 314 times as active, weight for weight, as radium. The comparison on the basis of gamma rays is more difficult, but it gives about the same figure, 300 to 500. Mesothorium is sold by a stated weight which is the weight of a gamma equivalent weight of radium. The amounts of the other active products, which,

with the exception of RaTh, have short half-lives, present in one gram of thorium, are also very small. Thoron, the gaseous emanation, decomposes into the solid ThA, giving the surface it condenses on induced radioactivity.

Table I
Uranium-Radium Series

Element	Symbol	At.Wt.	T Half Life	Relative Wt. in Equilib.	Rays	α-Ray Range in Air Cm. N.T.P.	Abs. Coeff. β and γ Rays Cm.$^{-1}$ Al
Uranium I	UI	238.18	4.5×10^{9} yrs.	2.94×10^{6}	α	2.53	.....
Ionium	Io	230	7.6×10^{4} yrs.	49	α	3.03	.....
					γ	....	1088; 22; 7; 0.41
Radium	Ra	226	1580 yrs.	1.00	α	3.21	.....
					β	....	312
					γ	....	354; 16.3; 0.27
Radon	Rn	222	3.82 days	6.5×10^{-6}	α	3.94	.....
Radium A	RaA	218	3.05 min.	3.54×10^{-9}	α	4.50	.....
Radium B	RaB	214	26.8 min.	3.05×10^{-6}	β	....	890; 80; 13.1
					γ	....	230; 40; 0.51
Radium C	RaC	214	19.7 min.	2.25×10^{-6}	α	3.6	.....
					β	....	50; 13.5
					γ	....	0.23; 0.127
Radium C′	RaC′	214	1.5×10^{-6} sec.	5×10^{-18}	α	6.60	.....
Radium C″	RaC″	210	1.32 min.	6×10^{-13}	β		
					γ		
Radium D	RaD	210	16 yrs.	9.4×10^{-3}	β	....	5500
					γ	....	45; 0.99
Radium E	RaE	210	485 days	7.8×10^{-6}	β	....	43
					γ	....	(45; 0.99); 0.24
Radium F (Polonium)	RaF	210	136.5 days	2.19×10^{-4}	α	3.72	.....
					γ	....	585
Radium G (U. Lead)	RaG	206	Stable	.....	.	....	.....

This table is condensed from tables of St. Meyer and E. Schweidler, "Radioaktivität," B. G. Teubner, 1927.

Thorium Series

Thorium	Th	232.1	1.65×10^{10} yrs.	2.6×10^{9}	α	2.58	.....
Mesothorium I	MsThI	228	6.7 yrs.	1.00	β	....	.....
Mesothorium II	MsThII	228	6.13 hrs.	1.05×10^{-4}	β	....	40-20
					γ	....	25; 0.116
Radiothorium	RaTh	228	1.9 yrs.	0.28	α	3.67	.....
					β	....	420
Thorium X	ThX	224	3.64 days	1.46×10^{-3}	α	4.13	.....
Thoron (Emanation)	ThEm	220	54.5 sec.	2.48×10^{-7}	α	4.74	.....
Thorium A	ThA	216	0.14 sec.	6.24×10^{-10}	α	5.39	.....
Thorium B	ThB	212	10.6 hrs.	1.67×10^{-4}	β	....	153
					γ	....	160; 32; 0.36
Thorium C	ThC″	212	60 min.	1.6×10^{-5}	α	4.53	.....
					.	....	14.4
Thorium C′	ThC	212	10^{-11} sec.	10^{-20}	α	8.17	.....
					β	....	.....
Thorium C″	ThC′	208	3.2 min.	2.88×10^{-7}	β	....	21.6
					γ	....	0.096
Thorium D (Th. Lead)	ThD	208	Stable	.....	.	....	.....

Summarizing, the α-ray activity of thorium is about 10^{-6} to 10^{-7} of that for radium, gram for gram, depending upon the amount of decay products present. The gamma ray activity is such that 6.85×10^{6} grams of thorium are gamma equivalent to one gram of radium while 19.0×10^{6} grams of thorium has enough equilib-

rium mesothorium to be gamma equivalent to 1 gram of radium (7). Thus roundly, a gram of thorium is about equivalent in its radioactivity to a microgram of radium.

A few words must be said about the uranium-radium series. From the table it may be seen that the amount of radium in equilibrium with one gram of uranium is about 3.4×10^{-7} grams (the usual Ra/U ratio). This appears to be much greater than the mesothorium/thorium ratio $1/2.6 \times 10^{9} = 3.84 \times 10^{-10}$ grams yet the radioactivity of uranium in equilibrium with its decay products is probably no greater than that of thorium when the figures of the preceding paragraph are recalled. From the data in the table it may also be deduced that one gram of radium produces 3.54×10^{10} α-particles or the same number of emanation atoms per second. The amount of radium emanation in equilibrium with one gram of radium can be shown to be 0.66 cubic millimeters (normal temperature and pressure conditions) corresponding to a weight of 6.5×10^{-6} grams for a monatomic gas of atomic weight 222. This emanation decays into further disintegrating products noteworthy among which is RaC from which powerful gamma rays are emitted.

The above description and discussion of the natural radioactive elements does not pretend to be complete and is given only to illustrate what properties the natural radioactive elements have to offer for this and similar technical problems.

The final point to be taken up in this review is that dealing with the detection of radioactive material once it has been introduced into a crack or void in the metal. The methods available are of two types: (a) photographic and (b) electrical methods. The advantages and disadvantages of each class will be discussed in turn.

Photographic Methods

The photographic plate has often been used as a means of measuring radiant energy and when properly used can yield results of precise value. Its advantages are that it is inherently quite sensitive and also that it integrates the radiation incident upon it making possible the detection and measurement of very weak sources.

To form an idea of the effectiveness of the photographic method some figures due to H. Przibram (8) are given in Table II.

Table II compares the photographic action of α, β, γ, and light rays in terms of the energy required to bring about changes in the

photographic negative. These figures show that from ten to a hundred times more energy per square centimeter is required for the detection of radioactive radiations than for ordinary light, but there are good reasons for this. For instance an α-particle may strike at most four or five silver bromide grains in the emulsion before its energy is absorbed by the gelatin. The figures above indicate reasonable

Table II
Sensitivity of the Photographic Plate to Different Kinds of Radiation

Nature of Action	α-Rays: Particles per Cm.^{2}	α-Rays: Energy Ergs/Cm.^{2}	β and γ-Rays Energy Ergs/Cm.^{2}	Light Energy Ergs/Cm.^{2}
Photographic threshold	$0.7–3.5\times10^6$	5.7–29	....	0.20
Satisfactory blackening	2.4×10^{11}	2×10^6	10^{10}	$0.7–2.3\times10^4$
Incipient overexposure	8×10^{11}	6.6×10^6	10^{10}	10^5
Complete overexposure	2.6×10^{12}	2.1×10^7	....	....
Negative reversal	4.7×10^{12}	3.9×10^7	....	....

sensitivity for α-particle detection. Photographic detection of a single α-particle is possible but the negative must be examined by microscope to find the streak produced by the α-particle. The threshold number (10^6/cm.^{2}) allows detection of fairly minute quantities of radioactive material if reasonable time for exposure is available. For a specific illustration, if one gram of thorium gives off 10^4 α-particles per second, a microgram will give 10^{-2} particles per second or only one in a hundred seconds. Suppose, however, that all the particles from this minute amount pass into one square millimeter of photographic film for ten days, or about 8.6×10^5 seconds. The number of particles emitted is 8.6×10^3 and their number per square centimeter 0.86×10^6, which is just on the listed threshold value. Granting that the figures are correct, such small amounts as one millionth of a gram of weakly radioactive material are photographically detectable due to their α-rays. If the radioactive material is carried in water or oil in such concentration that there are 100 mg./cm.^{3}, the volume occupied by the radioactive material, one microgram in weight, is 10^{-5}cm.^{3} or 0.01 cubic millimeter. This is about the volume of a fissure 0.01 millimeter wide, 1 millimeter long, and 1 millimeter deep, a crack of the type sometimes appearing between grains in photomicrographs.

In the above it was assumed that all of the α-particles emitted by a given weight of the radioactive material could reach the photographic film. This condition, of course, is not realized for several reasons. First, the α-particles are given off at random in all direc-

tions of space so that even if the photographic film is in direct contact with a source spread out in an infinitely thin sheet, only half of the radiation emitted can possibly pass into the film. Second, the α-particles and electrons are decidedly limited by even very thin layers of obstructions so that in a crack the particles ejected in deep lying material do not have any effect whatever, being stopped almost where they originate. Of course, this does not hold for gamma rays and very fast electrons but there again the effect on the photographic film is decidedly less than for α-particles.

On the other hand the absolute sensitivity of modern photographic film is far greater than is to be believed from the above work of H. Przibram. More recently G. L. Locher (9) has made a determination of the absolute sensitivity of Eastman Duplitized X-ray film for the $K\alpha$ X-radiation from zirconium (mean wavelength 0.7857 Å) by means of the Geiger-Müller counter. He found that the minimum exposure of X-ray film for detectable blackening is about 0.72×10^6 quanta per square centimeter. Converting this to energy per square centimeter by means of the quantum relation $E = h\nu$, we have 1.814×10^{-2} ergs/cm.^{2}, which is less by factors of ten to a thousand than the threshold values quoted in Table II. Of course, this value is for one particular kind of radiation and we do not know how the absolute sensitivity of X-ray film will change with wavelength and nature of the radiation.

It is not likely that the full theoretical capability of the photographic detection method can be realized in practice for the reasons given above, yet even if the method is less sensitive by a factor of a hundred less than estimated the method should still suffice to show up cracks of macroscopic size such as are revealed in magnetic powder methods.

Electrical Methods for Detecting and Measuring Radioactivity

Another method of detecting and measuring small amounts of radioactive substances is the electrical ionization method. This has certain advantages over the photographic method and it can perhaps be developed to the point where its absolute sensitivity is equal to or greater than that of the latter and the operating time requirements will be smaller. The electrical method is based on measurement of the amount of ionization of the atoms or molecules of air

or other gas through which the radiation passes. The ionization of the gas allows the passage of an electric current between electrodes placed in the ionized gas and the magnitude of this ionization current is thus a measure of the intensity of the radiation producing the ionization. Early workers measured the ionization by means of an electroscope since its rate of discharge measures the ionization leakage current. Modern methods of greater sensitivity employ ionization chambers which are essentially gas-filled chambers containing a pair of electrodes kept at some high, steady potential (usually 500 to 2000 volts). Ionization produced in the chamber causes a current to flow between the electrodes, which is measured by some sensitive device such as an electrometer or vacuum tube circuit. Apparatus of this type possess high sensitivity and is capable of recording the ionization produced by a single α-particle. Since one gram of thorium gives off about 10^4 α-particles per second a microgram will give off one particle in 100 seconds on the average, which is too little for certainty because momentary increase in the ionization current due to spurious causes as well as to α-particles may occur. If radium, which emits 3.7×10^{10} α-particles per second is used, a thousandth of a microgram will give off about thirty α-particles per second, which should be easily and definitely detectable by electric methods.

Since it is known that one α-particle generates 2.2×10^5 ion pairs it is easy to estimate the ionization current due to a gram of radium. Since radium emits 3.7×10^{10} α-particles per second, the total number of ion pairs produced is $3.7 \times 10^{10} \times 2.2 \times 10^5 = 8.14 \times 10^{15}$. If each ion carries one electronic charge (4.77×10^{10} e.s.u.), the ion current or charge generated per second is $8.14 \times 4.77 \times 10^5 = 3.88 \times 10^6$ e.s.u. per second. Since one ampere-second or coulomb is 3×10^9 e.s.u., the current in ordinary amperes is 1.29×10^{-3} amperes. The ionization current due to the α-particles of one microgram of radium is thus 1.29×10^{-9} amperes. Modern electrometer valve and galvanometer circuits can detect currents of 10^{-14} to 10^{-19} amperes. However, it is possible, by means of a high potential, to utilize the small amount of ionization caused by a single α-particle: $2.2 \times 10^5 \times 4.77 \times 10^{10} = 1.05 \times 10^{-4}$ e.s.u. $= 0.35 \times 10^{-13}$ coulombs to cause still more ionization and thus build up a heavy discharge which, once started, would continue indefinitely unless means for immediately ending it are provided. The Geiger and Geiger-Müller counters work on this principle. Thanks to research

in radioactivity the Geiger-Müller counter has become a useful and sensitive device. Essentially it consists of a pair of electrodes —a metal cylinder and fine wire placed along the cylinder axis —usually mounted in a glass tube containing some gas or even air at several centimeters pressure. A potential of several hundred to a thousand volts is applied through a high resistance, the wire being made the anode. An ionizing particle or quantum passing through the space between the electrodes may set up a momentary discharge which is quenched by the high resistance in series with the voltage supply. The pulse due to the discharge is communicated to the grid of a vacuum tube which amplifies it and passes it on to still more vacuum tubes as the need for amplification dictates. Although the Geiger-Müller counter is potentially capable of detecting the presence of a single ionizing particle or quantum of radiation actual counters are not 100 per cent efficient and sometimes record only a small fraction of the number of quanta passing through. Even this is high sensitivity and makes possible the detection of extremely small amounts of radioactive material and therefore also quite small defects.

The need for a Geiger-Müller apparatus suitable for field and routine work has led to the development of compact apparatus which is completely portable. A desirable accessory is a vacuum tube meter for indicating directly the average rate at which the pulses in the Geiger-Müller counter are being produced. Fig. 1 shows the completely portable outfit consisting of a sensitive Geiger-Müller apparatus designed by Dr. G. L. Locher and a simplified counting rate meter, designed by the writer, which gives a direct indication of counting rates as low as 20 per minute.

A point that has not been stated explicitly in the above discussion is that the effectiveness of a given radioactive substance is greater the shorter its half-life, that is, the greater its disintegration constant $\lambda = 0.693/T$ where T is the half-life in seconds. The number of disintegrations per second is always given by the fundamental relation $\frac{dN}{dt} = -\lambda N$ where N is the number of radioactive atoms present. This relation allows one to compute the number of ionizing particles emitted per second when the number of radioactive atoms is known. For an example we may return to the problem of estimating the radiations emitted from the radioactive atoms

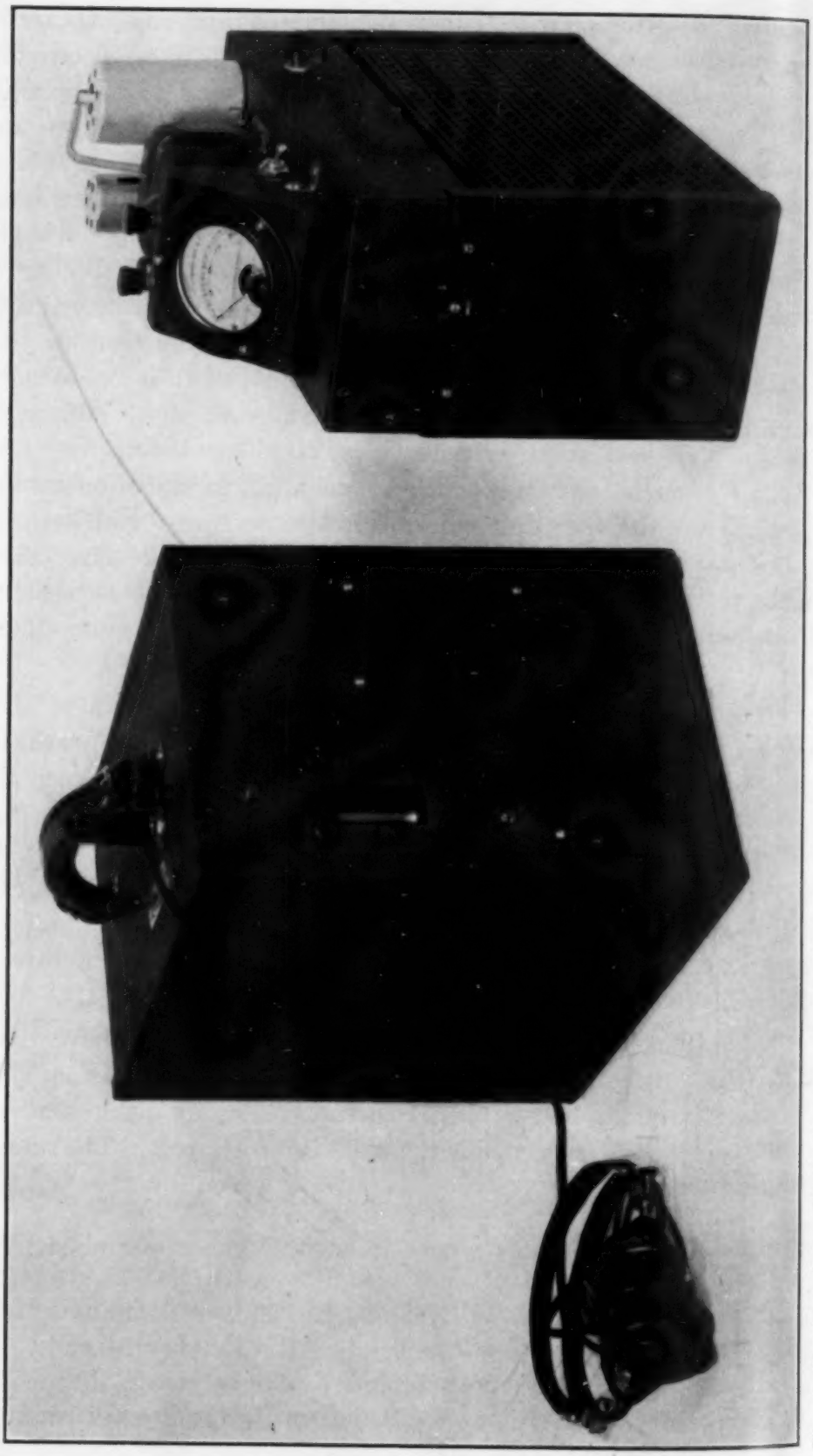


Fig. 1—Sensitive Geiger-Müller Counter and Simplified Counting Rate Meter for Detecting and Measuring Small Amounts of Radioactive Material.

contained in a crack having a volume of 0.01 cubic millimeters. This volume, it will be assumed, is completely filled with a radioactive fluid containing 0.1 milligram per cubic centimeter and thus will contain 10^{-9} grams of radioactive material. If this is radium, 10^{-9} grams will contain $\frac{10^{-9}}{226} \times 6.06 \times 10^{23} = 2.68 \times 10^{12}$ atoms and since the disintegration constant $\lambda = 1.30 \times 10^{-11}$ there will be $1.30 \times 2.68 \times 10 = 35$ disintegrations per second. Assuming that each disintegration is associated with the emission of a quantum of gamma radiation (as will be the case when radium is in equilibrium with its decay products) and also that only 0.1 of the quanta emitted will enter the counter tube this still leaves the appreciable number of 3.5 quanta per second or 210 per minute, which should be detectable even with a counter that is only 10 per cent efficient.

Finally, let an estimate be made of the effectiveness of the electric method when the crack of 0.01 cubic millimeter volume is filled with radon under normal temperature and pressure. The number of atoms contained will be $\frac{0.01 \times 10^{-3} \times 6.06 \times 10^{23}}{22400} = 2.71 \times 10^{14}$. The disintegration constant for radon is $\lambda = 2.085 \times 10^{-6}$, so the number of disintegrations per second will be $2.71 \times 2.085 \times 10^{8}$ or 5.65×10^{8}.

While this is an astonishing number of quanta to expect from so minute an amount of radioactive material it must be remembered that such an amount of radon represents the amount of radon in equilibrium with an appreciable and expensive amount of radium. Since 0.66 cubic millimeter of radon (N.T.P.) is in equilibrium with one gram of radium the above amount of radon is that which is in equilibrium with 0.01/.66 x 1000, or 15.2 milligrams of radium.

Nevertheless, the above figures excite the imagination with the possibilities they hold for the revelation of cracks and defects by means of radon, for even if, in the above example, the crack of 0.01 cubic millimeter volume is filled with air containing one atom of radon per million molecules of air the number of disintegrations per second should still be of the order of several hundred per second.

Before radon can be practically used for this purpose a number of practical difficulties must be solved. Radon decomposes into solid radioactive substances which are condensed on the surfaces of

Fig. 1—Sensitive Geiger-Müller Counter and Simplified Counting Rate Meter for Detecting and Measuring Small Amounts of Radioactive Material.

objects, giving them an induced radioactivity. Therefore in any practical application, technique must be developed for removing these decomposition products from the surfaces of the test piece where they will mask the effect of any radioactive material which is introduced into the cracks. Furthermore it hardly need be said that radon is very dangerous material to handle and a special technique must be developed to avoid completely the danger to the operator. Once such developments have been made there seems to be no reason why the radioactive method outlined and discussed in the preceding pages should not be capable of detecting almost any surface crack and possibly even internal defects in certain cases.

This will conclude the discussion of the possibilities in the use of radioactive indicator substances for the testing of metals. The remaining part of this paper will be given to describing some preliminary experiments carried out by the writer, utilizing the comparatively cheap and safe radioactive element thorium.

Experimental

Fluid Radioactive Sources

Thorium is commercially available in several compounds, the most common being the oxide ThO_2 and the nitrate $Th(NO_3)_4$. Unfortunately thoria, ThO_2, is an insoluble material and the production of a fluid radioactive material from it is out of the question. Thorium nitrate, on the other hand, is quite soluble and ideal for making a concentrated aqueous solution. As mentioned before, water as a fluid vehicle possesses characteristics none too suited for the purpose in hand. Oil, especially a light oil of the penetrating type, would be the more desirable fluid. Some attempts to get thorium salts into oil directly were not successful. Two possible ways, however, are open: (a) by formation of a thorium soap which will dissolve readily in oil, and (b) by the formation of a thorium phenyl compound similar to the lead tetraethyl employed in gasoline. It was found possible to make a thorium soap by adding liquid soap to a thorium nitrate solution at about 50 degrees Cent.; the precipitate or thorium compound was filtered off and dried in an oven at low heat. The dried soap was divided into 2-gram samples and numerous experiments were carried out to find a suitable solvent for the soap. Out of some 22 organic solvents tried, the only ones of promise were linseed oil, castor oil, and butyl butyrate, the last being the best. It was found that the thorium soap solution in

butyl butyrate could then be diluted with a light mineral oil known as ultrasene. The other possibility, that of using metal phenyl compounds, was not investigated since no thorium phenyl compounds were listed in organic chemical catalogs. Some experiments were also carried out on thorium soap prepared from thoria by conversion to its hydroxide and treated with hot solutions of stearic and oleic acids. The hydroxide was completely dissolved in the hot acid, but the stearic acid solution froze as expected on cooling. The solutions were tested for their solubility in light mineral oil (ultrasene) and it was found that only the oleic acid solution would remain clear on standing.

Table III

Material (1 Gram Sample)	Mean Discharge Time[1]	Notes
Thorium oxide	1 min. 5 sec.	(old stock)
Thorium soap	3 min. 25 sec.	1 mo. after preparation
Thorium hydroxide	2 min. 48 sec.	1 week after preparation
Conc. solution of thorium hydroxide in stearic acid	44 min. 31 sec.	Freshly prepared
Conc. solution of thorium hydroxide in oleic acid	69 min.	Freshly prepared
Blank test	104 min.	

[1]Over the arbitrary 100 sec. U scale of instrument.

The radioactivity of the various materials was tested by means of a good Kelvin electroscope of French make. The rate of discharge determines the activity of the sample. Table III gives the discharge times for certain radioactive materials worked on. The activity of the thorium soap seems to be fair as compared to thoria as a standard but that of the stearic and oleic acid solution rather poor. This may be expected for the weight concentration of thorium is probably less and the emission of α-particles is confined to the very outside surface layers.

Inspection Tests with Fluid Sources

A test of a radioactive oil for showing cracks in a shattered ½-inch zinc plate was carried out. The oil solution was made up as follows: 1.99 grams of the thorium soap as described above were dissolved in 20 cc. of hot butyl butyrate to which ultrasene oil was added until a solution was obtained which would remain clear when cooled to room temperature. With a total volume of 150 cc., the solution was clear and flowed freely when lukewarm.

The piece of zinc plate was placed in the warm radioactive oil

and left there about an hour. It was then removed from the oil and its surface rubbed dry, wiped with an alcohol sponge and finally rubbed dry again. This was done to make sure that the results obtained would not be due to any surface radioactive contamination. The piece was placed (in a dark room) in a light-tight can with pieces of Eastman X-ray film placed (a) bare on top of the piece and (b) below the piece covered by one thickness of white blotting paper. The arrangement, the test piece, and the films developed after an exposure of one month are shown in Fig. 2. Contrary to expectations, the upper film shows only a large blackened area about the size of the test piece, no particular cracks being indicated, only their general presence. The lower film shows a similar condition except for the small triangular area due to the accidental presence of a small piece of film on the under side of the blotter. The manner of blackening of the films suggests that the oil does not remain in the cracks, but creeps out over the surface of the test piece. In some respects this may be looked upon more as an advantage than a disadvantage, especially in case only the presence and approximate location of a defect is desired since the fluid creeping out to the surface may act more effectively on the photographic material. Experiments like the above were also carried out, using water solutions of thorium nitrate but the results in general were no better than those obtained with oil. In one instance individual cracks were revealed but the surface effect gave a very dark background.

Next, certain experiments were carried out to test the possibility of using plastic vehicles in which radioactive material can be carried in suspended form and quite high concentration. Accordingly, finely ground thoria was mixed into petrolatum jelly in the proportion of 1 gram of ThO_2 per cc. of petrolatum. This thorium oxide grease was then introduced into the cracks in test pieces by means of hydrostatic pressure. Fig. 3 shows a pressure bomb suitable for experimentation on small test pieces, the radioactive grease and the containers used for photography. The test specimens were packed in the pressure cylinder with enough thoria grease to cover them completely, the cylinder was then closed and pressure applied from a cylinder of compressed air. A pressure of 1000 pounds per square inch was maintained in the bomb for several hours. The test pieces were then removed and their external surfaces thoroughly cleaned with benzene, ether, and a dry cloth. Fig. 4 shows

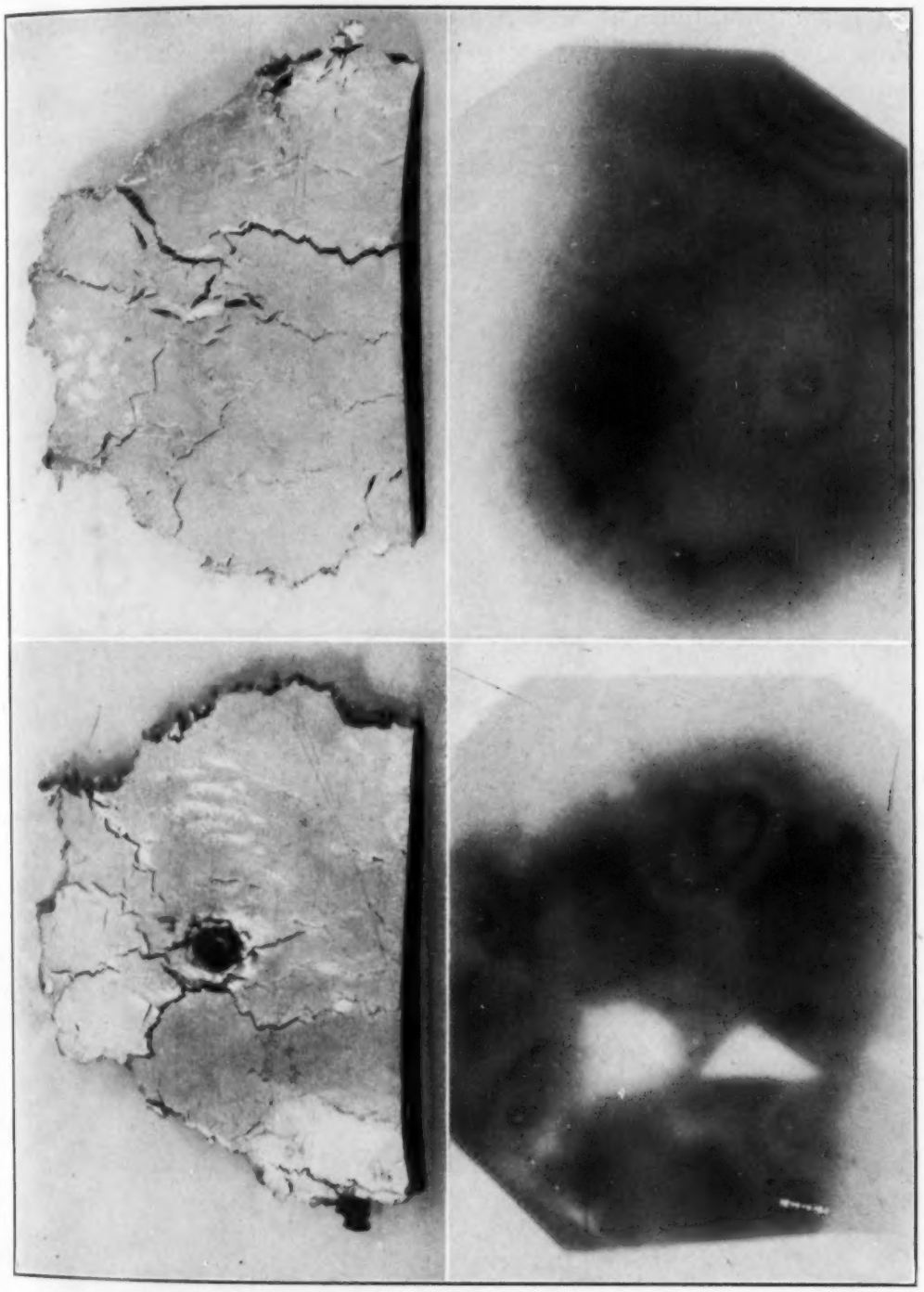


Fig. 2—Test of the Use of Radioactive Oil on a Shattered Metal Piece.

a piece of round bronze bar stock treated in the above way, the method of applying the film and the resulting radiograph. Fig. 5 shows a piece of zinc plate containing fine cracks, which was treated by the above described method, together with the radiographs of the

surfaces. The films in Figs. 4 and 5 were not used bare as in some previous experiments, but were wrapped in one thickness of black paper and were backed by lead. Exposures were for 6 days.

From Fig. 5, certain interesting conclusions may be drawn. In film (a) crack "i" is definitely indicated but not completely. Crack

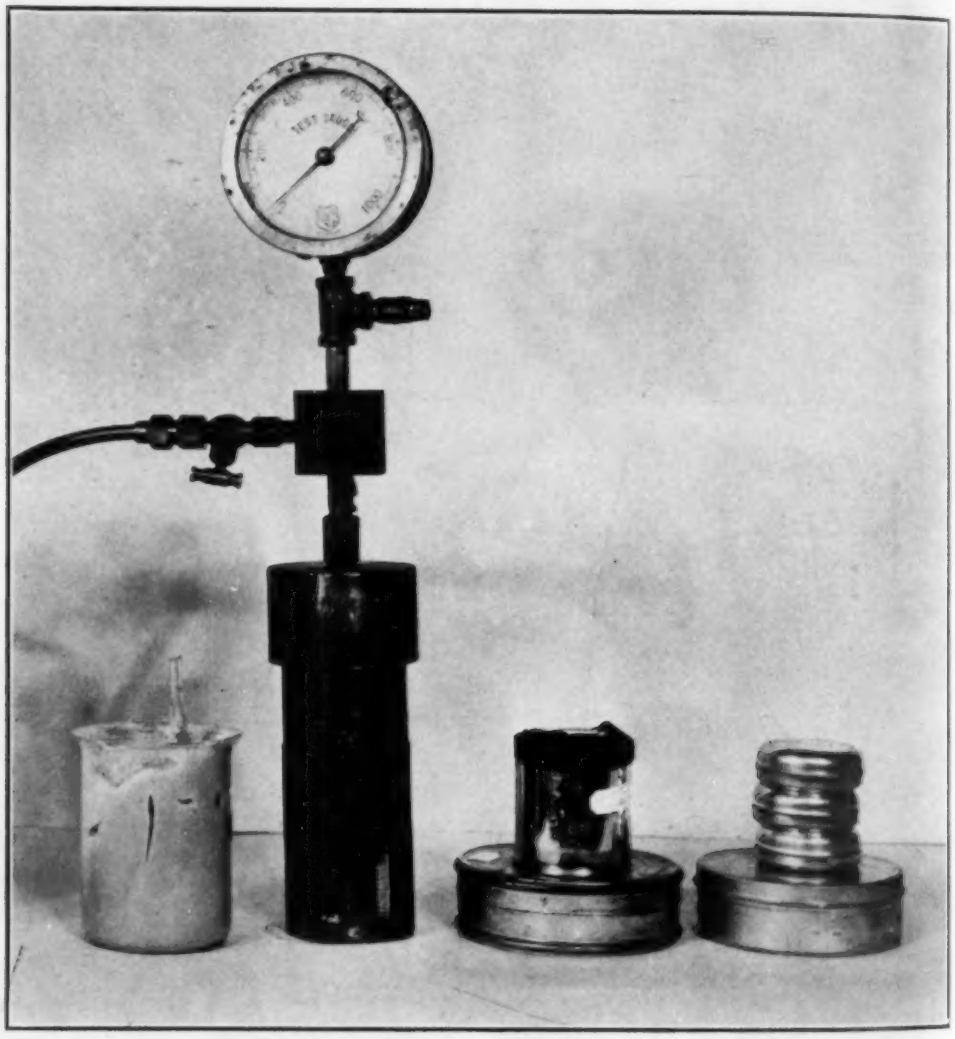


Fig. 3—Apparatus for Impregnating Test Pieces with Radioactive Grease.

"ii" about the same in length but much finer is not indicated. This leads one to believe that crack "ii" was not sufficiently supplied with radioactive material. Film (b) gives further reason to believe that this is the case. Cracks "i" and "ii" are well indicated by thick broad marks, but their continuations are represented only by two fuzzy spots. However, a fine hairlike crack V is indicated and perhaps others too. All in all the results indicate that the method can

show up quite fine cracks but that some are missed for reasons to be determined.

Possible reasons that may be advanced are (a) the distribution

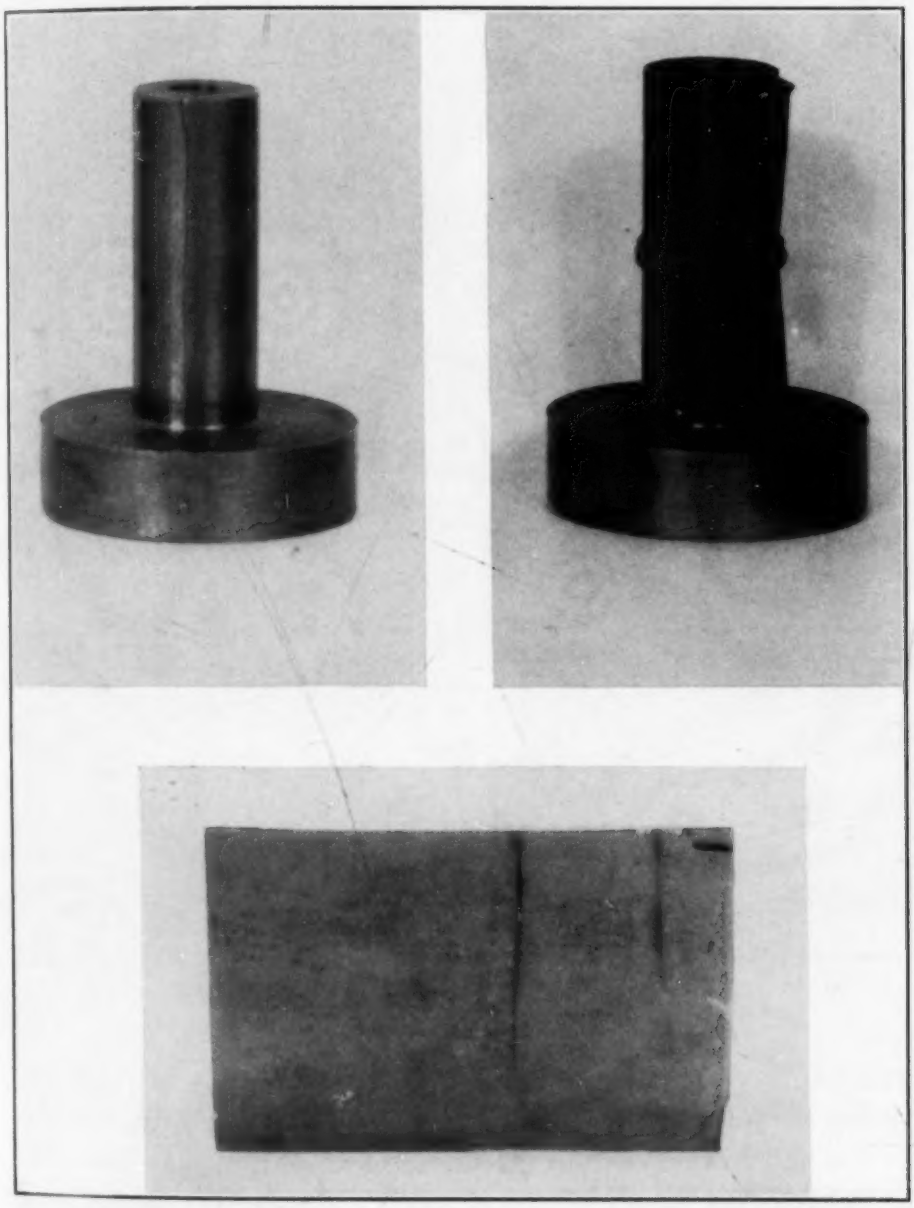


Fig. 4—Cracked Bronze Bar Stock and Auto-Radiograph of Cracks.

of the active material in the grease is not uniform, (b) the particle size of the active material might not be small enough to insure penetration into very fine cracks, (c) the film may not have been in close enough contact to register the extremely feeble radiation from

a minute crack, (d) the grease may not have been forced into a very fine crack at all.

In view of the encouraging results obtained, more work was undertaken attempting to improve the above described method. It is

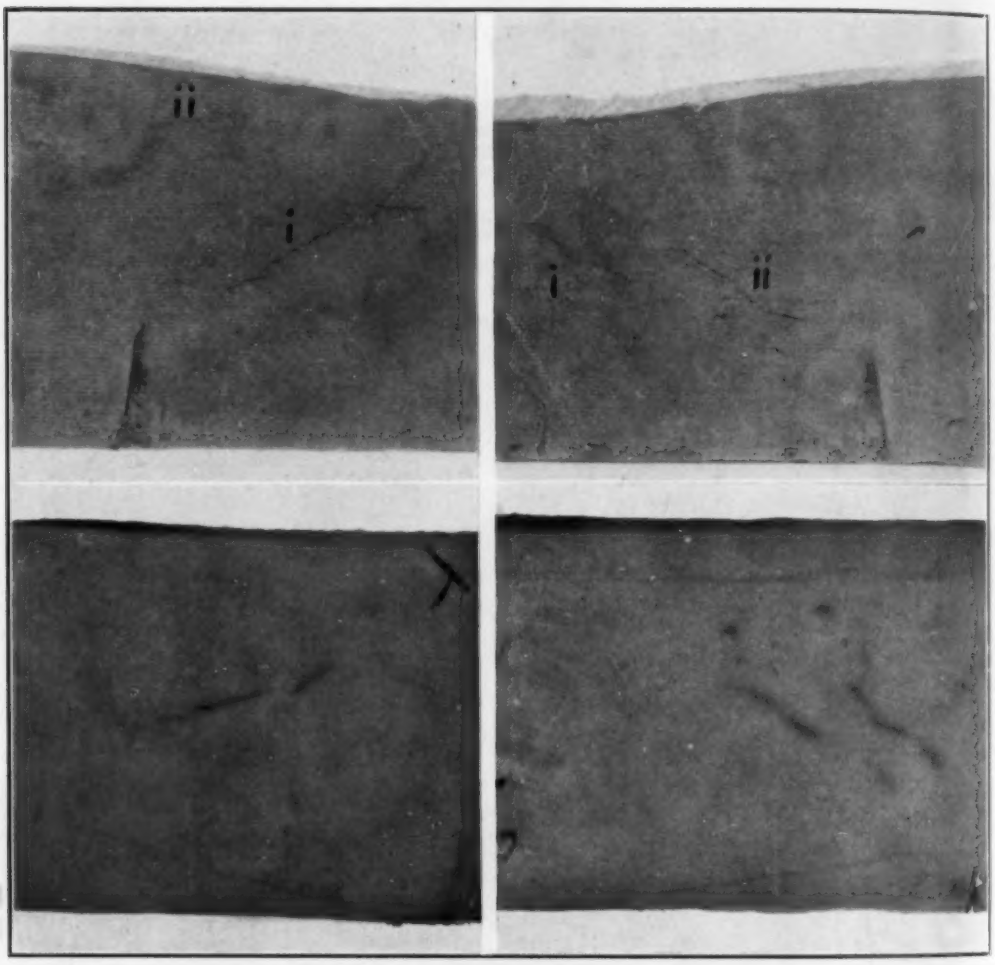


Fig. 5—Zinc Plate with Cracks and Auto-Radiographs.

beyond the scope and intention of this paper to describe all the experiments performed and contemplated in this connection, but the results obtained in one or two directions will be described before concluding this paper.

To study more quantitatively the effectiveness of the penetration of the thoriated grease into cracks, some artificial crack blocks were constructed. These are shown in Fig. 6. In Fig. 7 are shown radiographs obtained with them. By means of shims, the cracks may be made of any desired width. One of these artificial crack blocks was treated by the pressure grease method, using the 1 gram

per cubic centimeter thoria grease used in the cases illustrated in Figs. 4 and 5. Another of these blocks was treated using a grease of the same properties, but the thoria for which had first been ball-milled for several days and screened through 300 mesh screen to reduce the particle size of the thoria to a minimum. A third test block was treated with a grease made in still another way in which it is likely that the radioactive material is in colloidal form. Fifteen

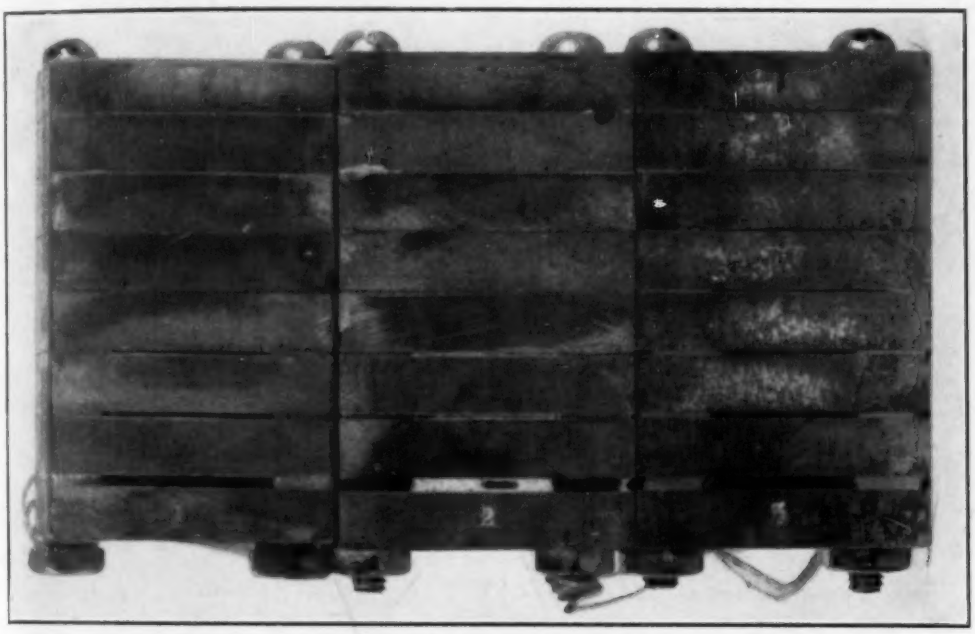


Fig. 6—Artificial Crack Blocks Containing Three Kinds of Radioactive Grease. No. 1. Ordinary Thoria Grease; No. 2. Ball-Milled Thoria Grease; No. 3. "Hydroxide" Grease.

grams of $ThNO_3$ were dissolved in water and converted to $Th(OH)_4$ by precipitating with NH_4OH. The soft colloidal precipitate was filtered out, partly dried and mixed with 75 grams of amber petrolatum. The grease was warmed and mixed for a day at 50 degrees Cent.

The three blocks were then compared by placing them together in one container, using an arrangement like that of Fig. 2 where one piece of film is placed bare on top of the test blocks and one piece covered with a single piece of black paper is placed below the block. The films were exposed for five days and then developed according to standard technique after these had first been thoroughly washed with an alcohol sponge to remove any grease from the films.

In Fig. 7 the upper photograph shows the bare film and the

lower the covered film. The effectiveness of the three kinds of grease is best compared by the latter, which shows that while ball milling may have made some slight improvement in the effectiveness of the grease, the best results were obtained from the grease in

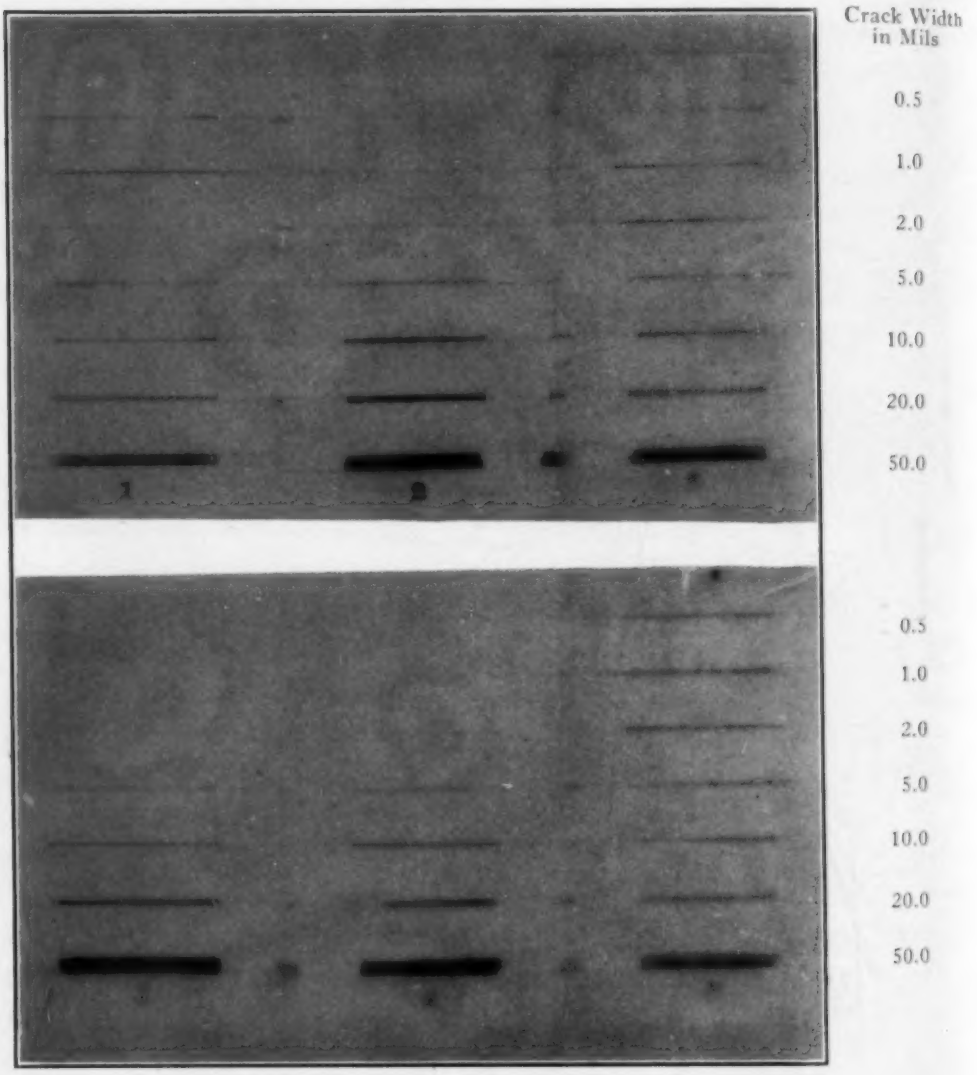


Fig. 7—(Upper) The Bare Film. (Lower) The Covered Film.

which the radioactive material is in a gelatinous or colloidal state. The actual concentration of thorium atoms in the "hydroxide" grease is somewhat less than in the other cases by the ratio weight $ThO_2/ThNO_3$, yet the effectiveness is decidedly better.

Some further possible ways of improving the thoria grease method are: (a) addition of certain fluorescent materials to increase the photographic effect of the thoria grease on bare film and

(b) improvement by selection or special treatment of a photographic material, film, or plate. Without going into details, it can be said on the basis of experiments carried out and under way that a certain amount of improvement can be obtained by the use of such fluorescent materials as calcium tungstate and barium platinocyanide and also that a comparison of ordinarily available photographic material has indicated that Eastman Duplitized X-ray film is decidedly the best for this particular purpose. In view of the fact that an α-particle strikes only four or five silver bromide grains before its energy is absorbed in the gelatin, it is not unlikely that a photographic material still better suited to this purpose could be developed. Plates of the Schumann type containing a high density of silver grains have not yet been tried by the author.

The above lines of improvement are of minor importance for it is obvious that the greatest improvement will come through the employment of more powerful radioactive materials. Since encouraging results have been obtained with such weak radioactive materials as thorium compounds, it should certainly be possible to effect vast improvement by the use of more powerful materials such as radium and radon. Work in this direction is under way.

Conclusion and Summary

In the above there has been an attempt to evaluate as completely as possible the possibilities in the use of radioactive material for the testing of metals for defects. Some disadvantages have been mentioned but not particularly stressed. In concluding it will be well to review certain objections that can be raised.

Chief among these is that the method of testing proposed may be dangerous, especially when strong radioactive materials are used, partly because of the radiations emitted and partly because of possible contact of the operator with the material itself. This danger is also partly present in the commercial radiography with radium but there it has been obviated and minimized by development of proper technique.

Another is that the method may be too expensive to be practical. From the quoted current prices of radioactive materials, it can be deduced that the necessary capital outlay for the testing of small metal parts will not be large. Furthermore, technique can be so developed that little or no radioactive material is wasted or lost.

The most serious objection that can be raised against the de-

scribed method is that it is practically limited to surface defects which can always be detected by visual methods. This remark could also be advanced against the use of the magnetic powder method for many of the defects located by it can be seen if an exacting scrutiny of the surface be made. While it is true that by suitable preparation of the surface any surface crack down to almost submicroscopic dimensions can be seen, the attendant work usually makes such a procedure time consuming and impractical. Sometimes it even happens that a deceptive surface marking is believed to be a crack.

Other objections might also arise based on technical difficulties which can be solved as the method is developed.

At the present time the proposed method of testing metal parts by radioactivity must be looked upon as a special method for research and for practical cases where other methods can be applied only with difficulty or not at all. It is practically limited to detection of defects reaching the surface of a test piece but can reveal at least the presence of these faults even when they may be in an inaccessible place in the object tested. A possible field for the radioactive method is the testing of small nonferrous parts of irregular and complicated shapes.

Summary

The possibility of using radioactive indicator substances in the detection of faults in metallic materials and finished articles has been studied and in general the possibilities offered by the natural radioactive elements are found to be quite promising. Certain disadvantages to be met are also discussed.

An experimental method utilizing the comparatively cheap and safe radio element thorium is described. It was found that water and oil solutions of the weakly radioactive thorium materials were not very promising but by incorporating thoria in grease in high concentration and applying this grease to a test specimen by means of hydraulic pressure enough radioactive material was introduced into the surface cracks to allow their detection by photographic film placed upon the surface.

Additional work on improving this method is outlined and briefly described.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Doctor R. H. Canfield, Superintendent of the Metallurgy Division of the Naval Research Laboratory, for his encouragement in this work; to Mr. Louis Singer, Assistant Chemist, U. S. Naval Research Laboratory, for his aid in the preparation of radioactive oils; to Mr. L. Philpott, Radio Division, U. S. Naval Research Laboratory, for his aid in the design of a counting rate meter; and to Doctor G. L. Locher, Bartol Research Foundation, Swarthmore, Pa., for much helpful information received.

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DISCUSSION

Written Discussion: By R. V. Lange, chief physicist, Radium Chemical Co., Inc., New York.

Mr. Kaiser presents a highly interesting procedure in radiography. While the idea of incorporating radioactive substances in oil or water has previously been used, this is apparently a new application of such material. Therapeutic preparations of radon in isopropyl alcohol or in petrolatum have been used in the treatment of some skin conditions. One of the major obstacles is the rapid loss of radon when the preparations are unsealed. Four hours after opening, the radon has practically all escaped from the carrier, and the only radiation obtainable is that from the decay products laid down while the radon was in the oil or alcohol. The inhaling of the escaped radon must be avoided.

We wish to point out, however, that extreme precaution must be exercised in making and using these preparations. Long deferred and unpredictable sequelae in the form of serious skin conditions have been known to result from contamination with even minute quantities of radioactive salves and solutions.

One might suggest the possible substitution of a nonradioactive fluorescent material, such as zinc sulphide, activated by ultra violet light for the recording of surface cracks on photographic film.

Written Discussion: By A. V. de Forest, professor, Massachusetts Institute of Technology, Cambridge, Mass.

This work is an interesting addition to the known schemes for detecting invisible cracks and may lead to important developments in this field. In general, it operates on the old theory of the oil and whiting procedure in which a solution is used which penetrates the crack and afterward the presence of the material in the crack is made visible. The limitation of the method comes about when the crack is too small to absorb the indicating liquid, or the amount of liquid exuded from the crack cannot be made evident by the sensitizing method used. The proposed use of radioactivity to locate the indicating fluid should provide great sensitivity.

In the case of rough and unfinished surfaces, a further limitation occurs when the irregularities of the surface retain a sufficient amount of indicating liquid to confuse the distinction between a surface irregularity and a small crack. Where the base material is magnetic, the well-known Magnaflux test seems to be completely successful in this respect, but in the case of nonmagnetic materials, further improvement in test methods is very much needed.

Another interesting possibility is in process of development in which the metal is coated with a quick-drying brittle film of lacquer, and a strain, usually derived from an impact loading, is applied to the part. The strain concentration, due to the crack in the underlying metal, causes a crack to form in the brittle lacquer coat. This crack can be readily seen from the light reflected from the edges. It has been found that this method can be made far more sensitive than the oil and whiting, in that no penetration of material into the crack is required. This test is being developed by the Magnaflux Corporation in conjunction with the magnetic method for ferrous materials.

There is certainly a great need for methods of locating small stress-raising cracks in many metal parts and any method which is useful in this field will add to the safety of engineering structures.

Written Discussion: By Gordon L. Locher, Bartol Research Foundation of the Franklin Institute, Swarthmore, Pa.

There can be little doubt that the application of radioactive methods to the testing of metals will increase in scope, because of some fundamental characteristics of radioactivity, itself. The activity of any given radioactive element depends solely on the quantity of the element present,—being independent of the state of physical or chemical combination, and unalterable by any process that can ordinarily be applied to the specimen containing it. Moreover, exceedingly minute amounts of radioactive elements are detectable by their radioactive emissions; the detection and comparative measurement of their activities do not ordinarily necessitate any damage to, or alteration of, the specimen in which the active material is contained. The recent decline in the cost of radium, the probability that numerous artificially radioactive elements will presently be available in usable quantities, and the development of unusually sensitive instruments for the detection and measurement of weak radioactivity, are practical factors that assure more extended applications of methods such as Mr. Kaiser has developed.

Mr. Kaiser's interesting method of detecting fissures and holes that connect with the surface of a slab of metal will undoubtedly have important appli-

cations. The observation, that fluid radioactive materials which have been forced into the fissures by gas pressure may subsequently come out again, increases the effective sensitivity of the method, since the weak radioactivity available is most easily detected when the active material is on an exposed surface. One might, indeed, purposely drive out most of the occluded active material, by the application of heat or vacuum, subsequently to the processes of injection and surface cleaning. Furthermore, an approximate measure of the mean porosity of the metal specimen (without regard to the location or kind of fissure) could be found by collecting and measuring the activity of the radioactive fluid which had first been injected into the specimen, and then expelled from it. It seems likely that at least part of the observed spontaneous emergence of the fluid material arises from the compression of gas trapped in the fissures and pockets of the specimen. If so, the injection of the fluid radioactive indicator could probably be facilitated by partial evacuation of the metal, before the active fluid was applied under pressure.

Choice of a method for detecting and measuring very weak radioactivity will naturally depend on such practical considerations as convenience and simplicity of the method, as well as the sensitivity of the detector. The relative importance of these factors can only be evaluated for specific problems, upon consideration of the practical conditions under which the tests must be carried out. Thus, the photographic method is relatively simple, and has a high integrating sensitivity, if the time available for the test is long enough. The highest sensitivity for detecting radioactive β- and γ-ray emissions is obtained with Geiger-Müller counter instruments, such as the one shown in Fig. 1 of Mr. Kaiser's paper. The high sensitivity of such an apparatus arises from the fact that it records individual ionizing particles that pass through its sensitive region, and individual β-particles liberated in the sensitive region by gamma-rays. In all other practical types of detector, more than one electronic particle (and usually many) must enter the sensitive region, in order that a detectable current may be obtained. Moreover, a counter apparatus, whether stationary or portable, is always at its maximum sensitivity, whereas other types of ionization-measuring instruments usually have to sacrifice sensitivity, when portability is required.

The consideration of some of the advantages and disadvantages of Geiger-Müller counters for the detection and measurement of weak radioactivity may be of interest here. The advantages include:

(1) The very high sensitivity and low inertia of a counter make possible the rapid detection of extremely minute amounts of radioactive material. This, in turn, diminishes the cost of the method, and minimizes the possible danger of radioactive contamination of personnel.[2]

(2) A counter apparatus always operates at its maximum sensitivity, and may be made in a portable form without any loss of sensitivity or dependability.

(3) Measurements made with a counter are quantitative; i.e., the readings obtained are directly proportional to the quantities of radiation falling on the sensitive region, provided that the "quality" of the radiation is the same throughout the measurements.

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[2]G. L. Locher and J. L. Weatherwax, *Radiology*, Vol. 27, 1936, p. 149-157.

(4) When extremely low intensities of radiation are to be measured, a counter apparatus may be used as an integrating instrument,—operating thus for any desired length of time. When larger intensities of radiation are available, the record may be given instantaneously, as with Mr. Kaiser's rate meter.

(5) Counters may be made in a wide variety of forms, suitable for the detection of β- and γ-radiations of different amounts and penetrations. Some forms can also be made for detection of α-particles. Possible disadvantages are:

(1) Since a counter apparatus is always operated at its full sensitivity, it cannot be used, unshielded, for measuring high intensities of radiations. This difficulty may be avoided, however, by changing the size of the counting tube to correspond to the intensity of radiation available, or by the use of suitable shields and diaphragms for controlling the admission of radiation to the tube.

(2) As with all other methods, except the photographic method, counters are not readily suitable for mapping the fine details of distribution of radioactivity in a very inhomogeneous source (such as a radioactive fluid in fine fissures and holes in a metal slab). One could, of course, use shields with very narrow apertures over the counter, but this would make the exploration of a surface slow.

(3) Most Geiger-Müller counters are not suitable for the detection of α-particles that are incident from outside the tube; and, in types that do admit α-particles, it is not always easy to distinguish these particles from β-particles and γ-ray recoil-electrons. For purposes of detection, such distinctions are unnecessary.

The β-ray efficiency of a counter such as that shown in Fig. 1 is very nearly 100 per cent, for β-particles that have enough energy to penetrate the wall of the tube (0.002 inch glass; air-equivalent of 15 to 18 cm., approximately). The γ-ray efficiency varies greatly with the wave length of the radiation, and lies between 1 per cent and 10 per cent, for γ-rays of radioactive origin. The tube does not admit α-particles. Typical responses of this type of counter to very weak point-sources of thorium, uranium, and radium, are as follows:

Source	Distance from Nearest Wall of Counter	Rate: Impulses Per Min.	Rate Due to 1 mg. of Material at 1 cm. Distance (Computed)
1.0 mg. Thorium	0.05 cm.	7.24	1.81
1.0 mg. Uranium	0.5 cm.	28.82	7.20
0.001 mg. Radium	50.0 cm.	34.1	$> 8.53 \times 10^3$

Since the "background counting rate" of this type of tube is about 5 impulses per minute, it is seen from the table that about 0.00014 milligram of radium, at 50 cm., gives a rate equal to the background rate. At $35 per milligram, 0.00014 mg. of radium is worth about one-half cent! At a distance of 1 cm., less than 1/2500 of this amount is required to double the background rate.

Written Discussion: By Charles S. Barrett, Metals Research Laboratory and Department of Metallurgy, Carnegie Institute of Technology, Pittsburgh.

It would be well to compare directly the sensitivity of the methods developed in this paper with simpler ones in which cracks are revealed simply

by the oil that seeps into cracks. A test that has been in use for some time, I believe, consists in filling the cracks with a thin oil, cleaning the surface and white-washing it, and then allowing the oil to flow out of the cracks by capillary attraction so as to make dark streaks on the white surface. The use of a vacuum or a pressure chamber might add to the sensitivity of the test, and though it would also add to the complexity, the method would still be cheaper and easier to use than a radioactive grease method.

Some recent experiences I have had with gamma rays in radiography show that photographic films may differ considerably in sensitivity to gamma rays even though they are of equal speed with X-rays. It would be important in studies like these to try all the available makes and styles of X-ray film, particularly the new Agfa Non-screen and Eastman No-screen films, if this has not yet been done.

Author's Reply

I appreciate Dr. Lange's remarks on the danger involved in the use of radon and radium and believe I have also pointed this out in my paper. The thorium grease preparations described, however, are so weakly radioactive that no danger need be feared from temporary contact of the skin with the grease. Dr. Lange's proposal to use fluorescent substances as crack indicators, while untested, seems to me to be up against the difficulty that in fine cracks the cross sectional area of fluorescent material will be so extremely small that the dim light that arises from the material will very likely escape notice.

In reply to Professor de Forest, I first want to congratulate him on his varnish method for locating cracks, which appears to be quite applicable in many cases. The ideal methods in crack detection, of course, are those which do not involve any special treatment of the test object, such as electromagnetic methods which in the course of time will be extended from magnetic to non-magnetic materials. Even electromagnetic methods will find limitations in their use, however, so that the art of defectoscopy will always rest on a variety of methods.

There are two advantages possessed by the radioactive method that I did not point out in the oral presentation. The first of these is that filling a crack with radioactive material of known strength provides a means of determining almost quantitatively the magnitude of this crack. Many methods indicate the presence of a crack, but very few can give even roughly the depth or magnitude of a crack. The second possible advantage is that the method promises a means for testing inaccessible places in a metal piece, for radioactive fluids can be run into these places and flushed out again, except for that absorbed by the cracks present.

Dr. Barrett's suggestion that a direct comparison between the oil whiting test and the radioactive method be made is a good one, and awaits doing. Offhand, it seems that the oil whiting test will be limited by the fact that a certain amount of oil must come out of the crack to cause the least perceptible blackening, while the radioactive method depends mainly on the concentration of radioactive atoms in the oil or fluid which concentration can be arbitrarily altered.

Several kinds of photographic films were tried, among them Superpan Press, but nothing superior to Eastman X-ray Duplex for this sort of work was found. It is not likely that any better material may be found, except perhaps in plates of the Schumann type, where the density of silver granules is increased greatly.

I am glad to note that Dr. G. L. Locher shares my belief that radioactive substances will find increasing use in practical applications, and that he has made several suggestions whereby the proposed method of testing may be improved. As he has pointed out, the Geiger-Müller tube gives us a means for quickly detecting and even measuring very minute amounts of radioactive substances. The presence of a background counting rate due to cosmic radiation and spurious causes is not a serious objection. If it were possible to develop a counter tube responding only to α-particles it could possibly be used in an instrument which would indicate not only the presence of a surface crack containing radioactive material, but also its position. The writer has found that due to the action of the inverse square law, even the conventional Geiger-Müller tube will approximately locate a small crack containing a minute amount of radioactive material.

THE PRODUCTION OF FLAKES BY TREATING MOLTEN STEEL WITH HYDROGEN AND THE TIME OF COOLING NECESSARY TO PREVENT THEIR FORMATION

By R. E. Cramer and E. C. Bast

Abstract

A brief review of recent literature on flakes in steel shows that many metallurgists are associating the development of flakes with the presence of hydrogen in the steel.

One recent experiment is described in which large ingots of open-hearth steel were treated with hydrogen and "control specimens" rolled from these ingots developed many flakes. A system of experimentally slow cooling other specimens from the same bars gives information on the time of cooling necessary to prevent the formation of the flakes, and the temperature at which the flakes formed. Conclusions are drawn which would apply only to the bars used in this experiment.

Flakes Produced with Hydrogen

FLAKES in steel were first produced experimentally about three years ago by treating molten steel with hydrogen as reported by Bennek, Schenck and Muller (1).[1] This knowledge of a treatment which will produce flakes gives us a useful method of making steel to use in studying the rates of cooling necessary to prevent the formation of flakes. In 1936 when a paper (2) was presented by one of the writers at the A.S.M. Convention there was considerable skepticism expressed as to whether hydrogen could be the chief cause of flakes in steel. Since that time a considerable number of articles in the literature have given more information on the development of flakes. Some of these will be briefly reviewed.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, R. E. Cramer is special research assistant professor in engineering materials and E. C. Bast is test assistant, engineering experiment station, University of Illinois, Urbana, Illinois. Manuscript received June 23, 1938.

Brief Review of Recent Literature

Guichard, Clausmann and Billon (3) report that hydrogen forms water vapor with the oxides contained in steel thus developing enough pressure to form flakes. Schell (4) believes that shatter cracks in heat treated steel form after the last reversal in internal stress which occurs during cooling nearly at room temperature. He recommends repeated hardening as useful in studying shatter cracks. Maxwell (5) states that hydrogen causes embrittlement due to grain boundary attack. Drescher and Schäfer (6) melted steel under hydrogen and found it reduced the ductility of the finished steel. Ploum (7) explains how steel can dissolve atomic hydrogen.

Bardenheuer and Keller (8) give information regarding hydrogen causing steel to be hot-short and low in notch toughness. Delbart (9) classifies different grades of steels, which are likely to flake, according to their cooling curves and points out the effect of thermal strains and local heterogeneities in the formation of flakes. Musatti and Reggiori (10) give reasons why flakes seek a zone intermediate between the surface and center of steel bars.

Yajima (11) gives the distribution and diffusion of hydrogen in ingots. Honda and Hirone (12) have furnished a mathematical calculation of the pressure developed in elongated cavities during the cooling of steel containing dissolved hydrogen. They find that a theoretical maximum pressure of 500,000 pounds per square inch could be developed in a small cavity at 500 degrees Fahr. (260 degrees Cent.). Klausting (13) writes on conditions leading to flake formation and states that flakes may require eight hours time to develop after the bars have cooled to room temperature. Pihlstrand (14) exposed finely divided iron to hydrogen at different temperatures and found the effect of carbon, manganese and silicon content on the amount of hydrogen dissolved by steel. Norton (15) uses vacuum tubes to study the flow of hydrogen through steel at ordinary temperatures. Iwase and Fukusima (16) have developed a special method of measuring solubility of hydrogen in metals and applied it to ten metals and eight binary iron alloys.

Hare, Peterson and Soler (17) developed a very novel and useful method of determining the hydrogen content of molten steel and give data on several heats of steel. Their analyses show that there is a continual absorption of hydrogen during the time the molten steel is in the furnace except for periods when the heat is being worked.

The amount of hydrogen in the steel is highest at the time of tapping the heat. These authors also give information on 127 heats of steel made throughout the year which show higher hydrogen content during the warmer months and suggest that this may be associated with the moisture content of the air during this period. Bamford (18) gives a very complete summary of hydrogen in steel, including a discussion of the pressures developed in cavities, the embrittling effect of hydrogen, the possibility of rusty scrap, burnt lime and ferro-alloy additions introducing hydrogen into molten steel and a warning that more attention should be given to the possible presence of hydrogen in steel. Graham and Work (19) emphasize the possibility of iron absorbing hydrogen from the moisture content of the air used in the blast furnace and open-hearth furnace. This brief mention of only a part of the recent work which has been reported on flakes and hydrogen in steel shows the attention being given to this subject. To one not familiar with the subject the last three articles mentioned would give a good introduction to the subject of hydrogen in steel.

Extent of Experimental Work

During the last two years the writers' interest in this subject has been chiefly in determining quite definitely the condition of slow cooling necessary to eliminate flakes in steel bars whose heaviest section measures 1½ x 3 inches. The work recently completed has consisted of obtaining, and testing for the presence of flakes, 90 experimentally box-cooled specimens from six heats of steel, half of which had been treated with hydrogen, as explained below, in order to insure the presence of flakes in the test specimens. This work was made possible through the generous co-operation of the Dominion Steel and Coal Corporation, Ltd., Sydney, Nova Scotia. In order to locate flakes, a 6-inch longitudinal section of each specimen was sliced into three slices and the slices macro-etched in hot 50 per cent hydrochloric acid.

Method of Treating Ingot with Hydrogen

The ingot molds used were 90 inches high holding about 5 tons of steel. The steel used was open-hearth carbon steel varying in carbon content from 0.66 to 0.77 per cent and in manganese content from 0.63 to 0.87 per cent. The method of introducing hydrogen is

shown in Fig. 1. Most of the details of the method of adding the hydrogen were worked out by H. B. Wishart and associates of the Department of Metallurgy, Carnegie-Illinois Steel Corporation, Gary, Indiana. The hydrogen gas from the cylinder is bubbled through a bottle containing mercury in order to know when the gas is flowing. The rubber stopper was wired in and the bottle tested to 40 pounds

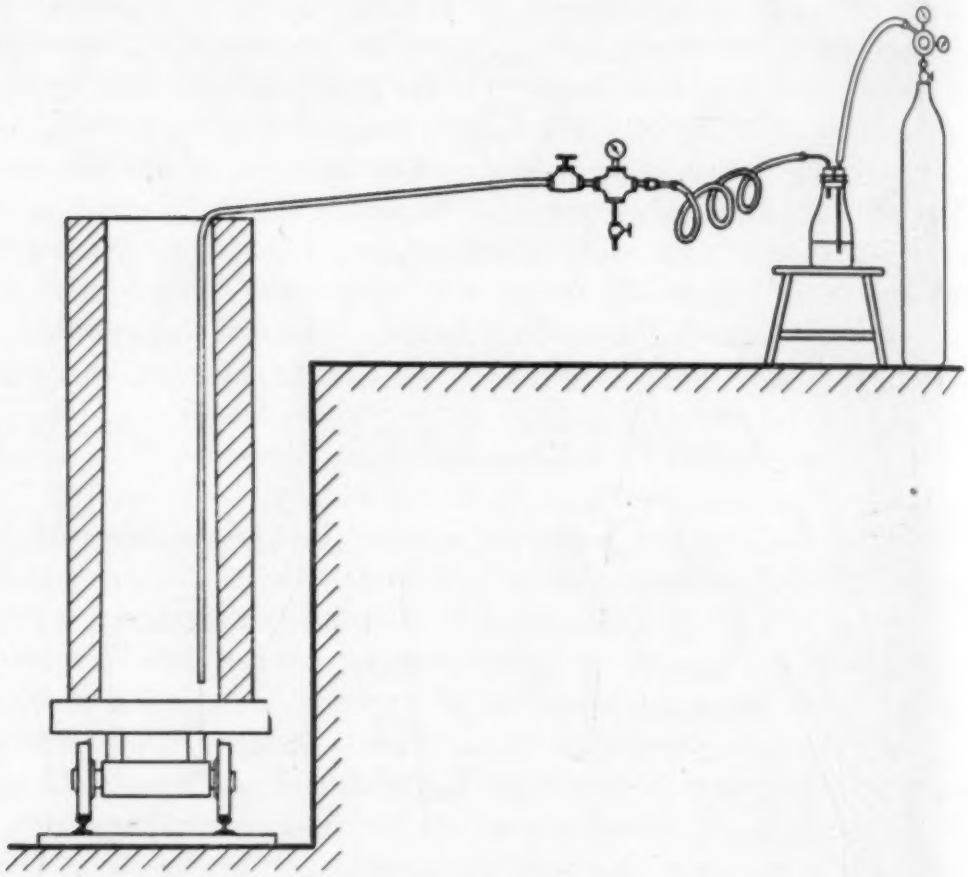


Fig. 1—Sketch of Method of Treating Ingot with Hydrogen.

pressure. For safety it was partly buried in a box containing cleaning waste during use. The bent ¼-inch "double extra strong pipe" has a wall thickness of about ¼ inch which requires some time to melt off as the molten metal rises in the ingot mold. The hydrogen was lighted at the end of the pipe before starting to pour the ingot and a pressure of 15 pounds per square inch was used when the first metal entered the mold to keep the end of the pipe open. The hydrogen pressure was increased as the metal rose in the mold to keep an even flow as indicated by the bubbling gas in the bottle, and the pipe

was moved back and forth across the mold in the molten steel. A maximum pressure up to about 30 pounds per square inch was necessary depending on how fast the pipe melted away. It was found advisable to stop the flow of the hydrogen when the metal was about one foot from the top of the mold to keep the molten metal from being thrown out of the mold. The pipe was usually two or three feet long when removed from the metal depending on how fast the ingot was poured. The time of pouring was varied from 2 to 4 minutes and this also governed the volume of hydrogen used, the latter varying from 30 to 70 cubic feet. While freezing, the metal gave off considerable hydrogen which burned at the top of the ingot. In the case of one ingot the solid crust was burned through with an oxygen jet resulting in a ½-inch stream of molten steel being thrown 5 or 6 feet high for about a half minute showing that considerable internal pressure was being developed as hydrogen and other gases were liberated during the solidification of the steel.

Method of Controlling the Rate of Cooling of Specimens

In order to study the effect of slow cooling on the development of flakes, the following procedure was used. Fourteen or more specimens, two feet in length, were cut from one bar, at the hot saws, in about five minutes. A specimen from each end of the bar was cooled in open air, one on the mill floor and the other by setting across two supports. These are considered as "control specimens" to determine the tendency of that bar to develop flakes. The remaining twelve specimens were divided into three groups of four each and allowed to cool on the mill floor to 900 degrees Fahr. (480 degrees Cent.) at which temperature two groups were placed in the cooling boxes shown in Fig. 2, packed in rock wool insulation and thermocouples attached. The numbering system used for the specimens consisted of three numbers, the first indicating the test run, second the ingot number and the last the position of the specimen in the bar as 3-2-1.

The boxes used for specimens 1 to 4 were packed with varying amounts of the insulation so that the specimens would cool at different rates. The boxes used for the second set of 4 specimens were filled with insulation and the specimens removed from the boxes at temperatures of 800, 700, 600 and 500 degrees Fahr. (425, 370, 315 and 260 degrees Cent.). The third set of four specimens was cooled on the mill floor to temperatures of 500, 400, 300 and 200 degrees

Fahr. (260, 205, 150 and 95 degrees Cent.) at which temperatures the boxes were filled with the rock wool insulation. Cooling curves for a typical test are shown in Fig. 3.

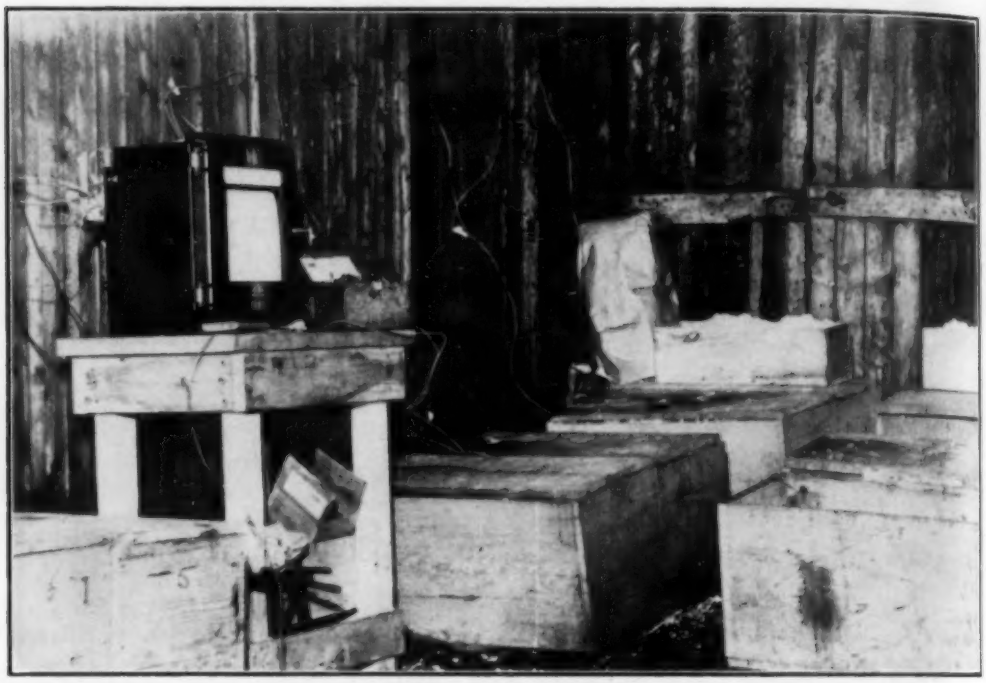


Fig. 2—Apparatus Used for Cooling Specimens. Photograph Shows a Portion of the Cooling Boxes, 12-Point Temperature Recorder and Thermocouple Attached to One Bar.

Cooling temperatures were recorded on all specimens with a 12-point recorder using No. 22 gage asbestos covered chromel-alumel thermocouples clamped on the specimens under a block of asbestos which held the couple junction tightly against the steel. Laboratory tests had previously showed good agreement between temperatures recorded in this manner and those measured by a thermocouple placed in a hole drilled into the same bar.

Results of Etch Tests of Specimens

As stated above the specimens from each bar were divided into three groups cooled approximately as shown in Table I. This table also gives the number of longitudinal or transverse flakes found in each slice six inches long cut from the bars from one hydrogen-treated ingot. The cooling curves for these particular specimens are those shown in Fig. 3. This ingot developed the greatest number of flakes in the control specimens of any bar out of 1100 previously

tested by the writers. However, when a bar contains a large number of flakes they are not as large as in those containing a medium number. Photographs of three of the specimens reported in Table I are shown in Fig. 4 in which (a) is the specimen cooled in 59 minutes, (b) cooled in six hours, four minutes, and (c) cooled in a "Mackie tank" designed to prevent the formation of flakes.

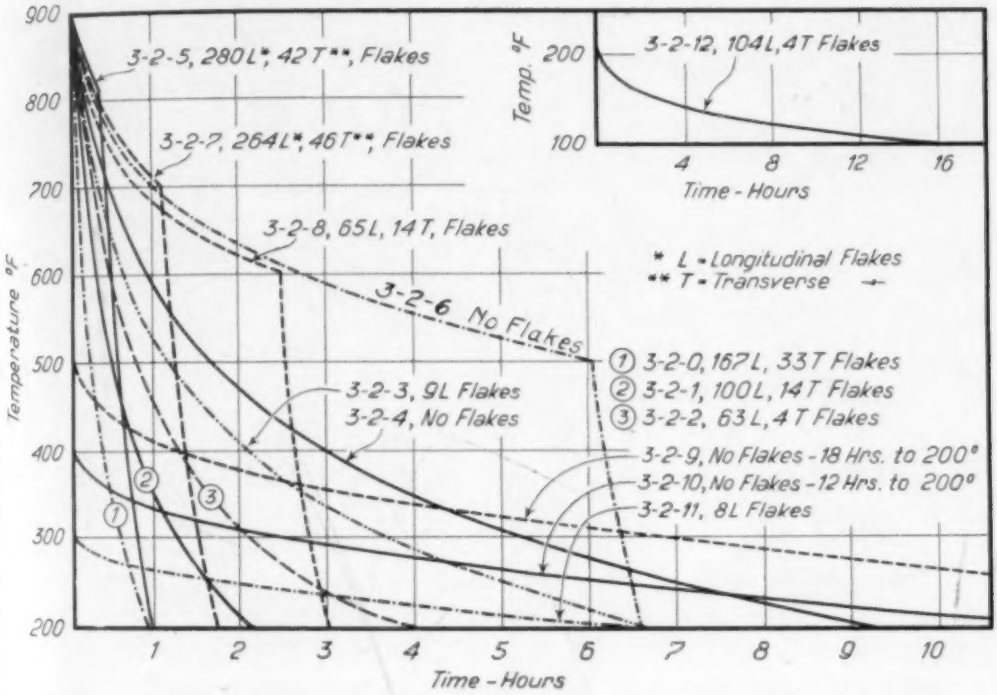


Fig. 3—Cooling Curves of Specimens. Test 3 Ingot Treated with 70 Cubic Feet of Hydrogen. L=Longitudinal Flakes; T=Transverse Flakes.

The time of cooling and the number of flakes found in all 90 specimens from the six heats of steel tested are shown in Table II. As indicated in the table, the ingots from which three bars were rolled were treated with hydrogen and the control specimens, whose last number is always 0 (as 2-6-0), from these three ingots contain many more flakes than the three ingots not treated with hydrogen. In fact these three untreated ingots were the only ones out of 11 untreated ingots tested which developed any flakes. It will be noted under the "Specimens Cooling at Different Rates" that flakes were eliminated in untreated ingots when the time of cooling from 900 to 200 degrees Fahr. (480 to 95 degrees Cent.) was three hours, 46 minutes for one test and five hours, 26 minutes for another. While with the hydrogen-treated ingots six hours, 11 minutes and nine hours, 11 minutes, respectively, were required for two of the ingots.

Under the specimens taken out of the cooling boxes at different temperatures, it will be noted that flakes are eliminated by varying the amount of time from four hours, 35 minutes to seven hours, eight

Table 1

Method and Time of Cooling and Flakes Found in Specimens from one Heat of Steel

Test No. 3, Ingot No. 2			Treated with 70 cu. ft. of Hydrogen		
		Time from 900° F. to 200° F.	†Flakes on One Side of 6-inch Slice		
Spec. No.	Method of Cooling	Hr. Min.	Slice 1	Slice 2	Slice 3
	Control Specimens Cooled as Indicated				
3–2–0	Hot bed	0 59	165 L, 25 T	167 L, 33 T	180 L, 10 T
3–2–13	Hot bed	No record	112 L, 28 T	172 L, 36 T	195 L, 30 T
3–2–14	Mill floor	No record	130 L, 18 T	135 L, 50 T	175 L, 25 T
3–2–15	Outdoors	No record	265 L, 70 T	310 L, 50 T	300 L, 46 T
3–2–16	Mackie tank	17 25	0	0	0
	Series Cooling at Different Rates (Put in at 900° F., Out after 20 hours)				
3–2–1		2 07	4 L,	100 L, 14 T	80 L, 6 T
3–2–2		3 56	15 L, 1 T	60 L, 4 T	63 L, 4 T
3–2–3		6 38	0	9 L,	5 L,
3–2–4		9 11	0	0	0
	Series Out of Boxes at Different Temperatures (Put in at 900° F. then cooled outdoors)				
3–2–5	800° F.*	0 21	168 L, 35 T	215 L, 36 T	280 L, 42 T
3–2–7	700° F.*	1 08	39 L, 6 T	264 L, 46 T	223 L, 33 T
3–2–8	600° F.*	2 29	0	65 L, 14 T	65 L, 9 T
3–2–6	500° F.*	6 04	0	0	0
	Series Put in Boxes at Different Temperatures (Out after about 20 hours)				
3–2–9	500° F.**	17 57	0	0	0
3–2–10	400° F.**	11 36	0	0	0
3–2–11	300° F.**	6 27	2 L,	8 L,	8 L,
3–2–12	200° F.**		31 L, 1 T	104 L, 3 T	104 L, 4 T

†Flakes are recorded as the number of Longitudinal (L) or Transverse (T) flakes on one side of a horizontal slice 6 inches long.
*Temperature on removing from cooling box and set outdoors at temperature of 30° F.
**Temperature on placing in cooling box.

minutes in the hydrogen-treated ingots. The series of specimens put into boxes at different temperatures were designed to furnish information on the temperature at which flakes developed. It will be noted that only one hydrogen-treated specimen developed flakes while cooling in air above 300 degrees Fahr. (150 degrees Cent.) while all specimens but one developed flakes before cooling to 200 degrees Fahr. (95 degrees Cent.). Macrographs of three other specimens are shown in Fig. 5 showing in (a) large flakes in a hydrogen-treated specimen, (b) large flakes in a specimen not treated with hydrogen and (c) specimen from same bar as (b) in which flakes were eliminated by cooling from 900 to 200 degrees Fahr. (480 to 95 degrees Cent.) in three hours, 21 minutes.

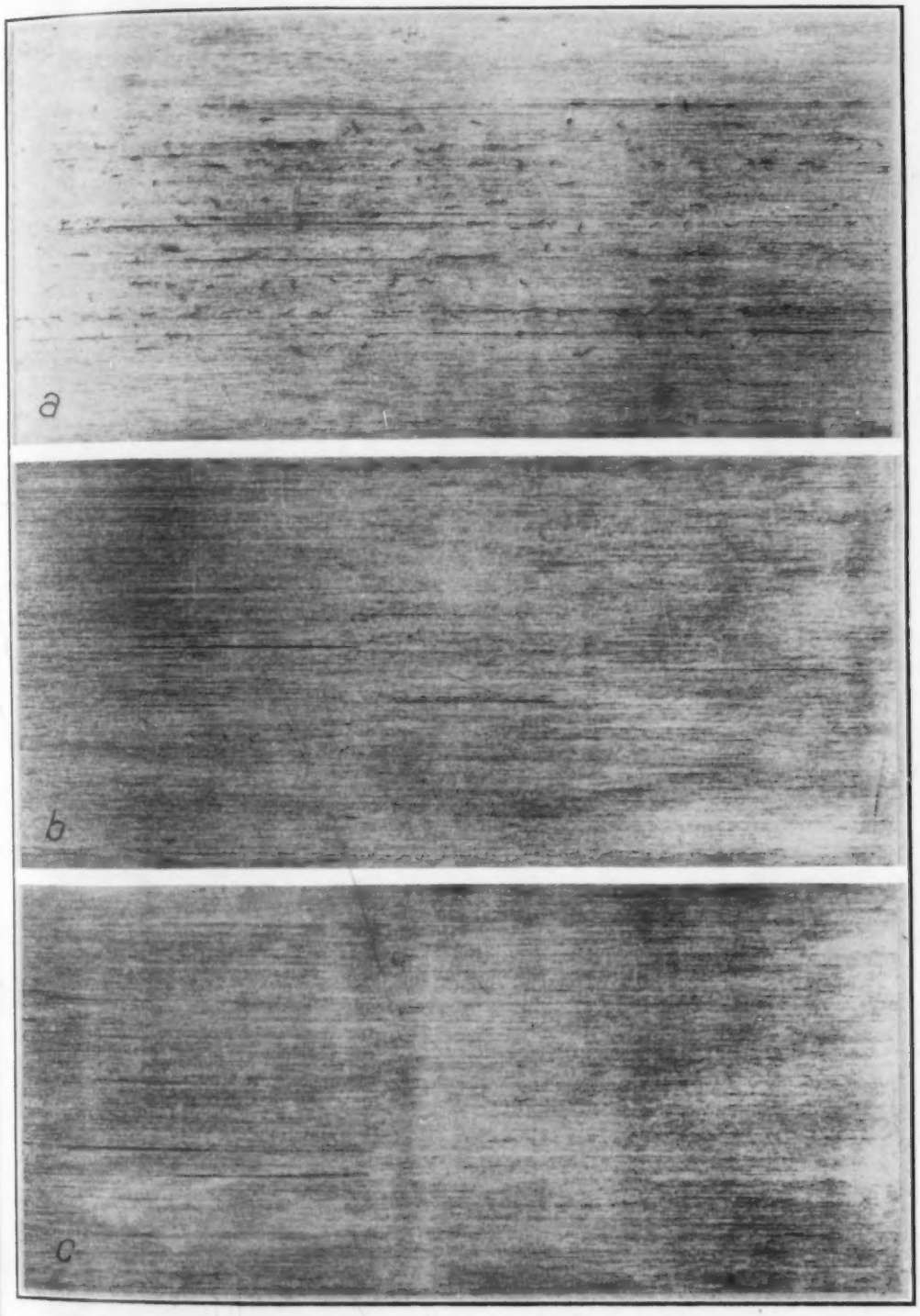


Fig. 4—Etch Tests of Three Specimens from Test 3. Etched Approximately 1 Hour in Hot 50 Per Cent Hydrochloric Acid Solution. Approximately ¾ Natural Size.

(a) Control Specimen No. 3-2-0 Cooled in 59 Minutes Containing 167 Longitudinal and 33 Transverse Flakes.

(b) Specimen 3-2-6 Cooled from 900 Degrees Fahr. to 200 Degrees Fahr. (482 Degrees Cent. to 93 Degrees Cent.) in 6 Hours and 4 Minutes Which Prevented Flakes from Forming.

(c) Specimen 3-2-16 Cooled in a "Mackie Tank," Designed to Prevent Flakes from Forming, and this Method was Successful.

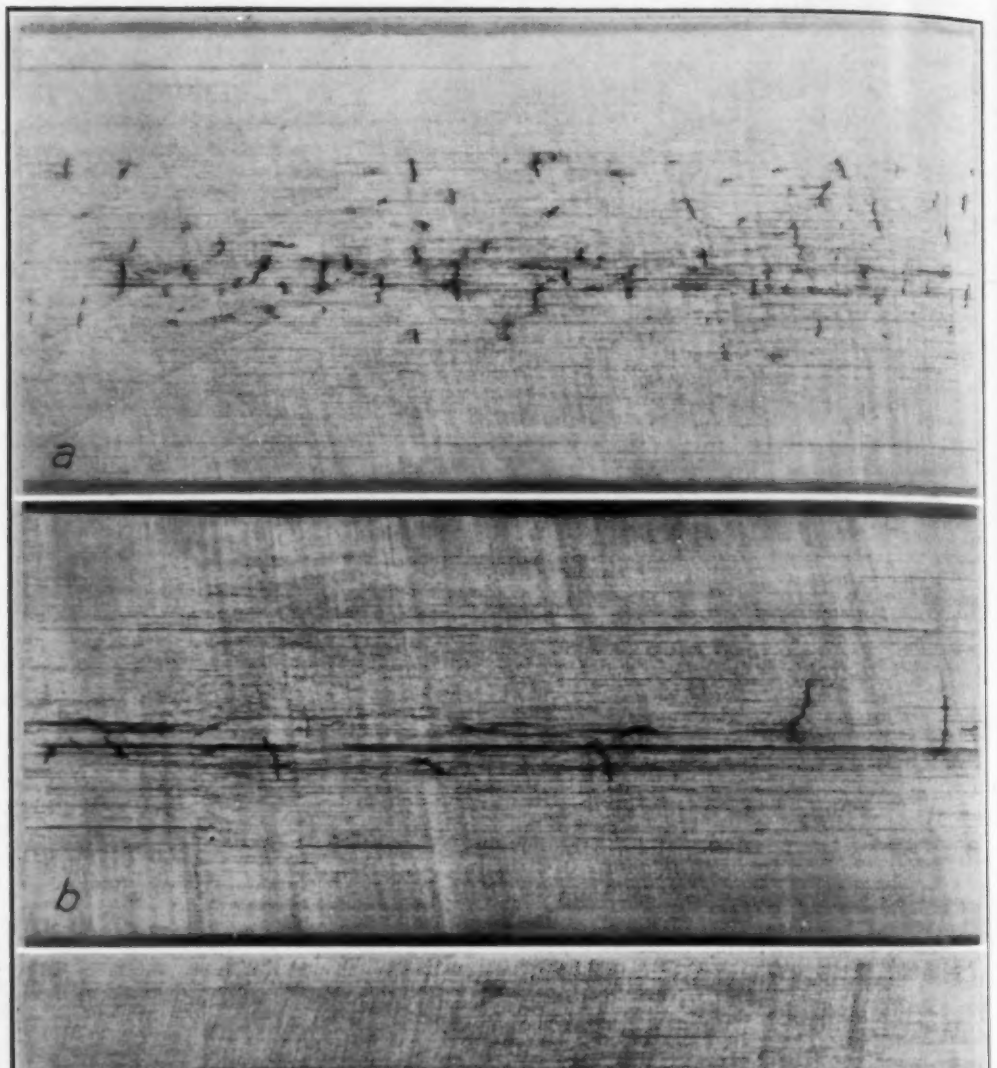


Fig. 5—Etch Tests of Two Specimens with Large Flakes. Etched Approximately 1 Hour in Hot 50 Per Cent Hydrochloric Acid Solution. Approximately ¾ Natural Size.
(a) Large Flakes in Hydrogen Treated Specimen No. 12-3-0.
(b) Large Flakes in Specimen No. 6-2-0 Not Treated with Hydrogen.
(c) Specimen from Same Bar as (b) No. 6-2-5 in Which Flakes Were Eliminated by Cooling from 900 Degrees Fahr. to 200 Degrees Fahr. (482 Degrees Cent. to 93 Degrees Cent.) in 3 Hours and 21 Minutes.

Table II
Method and Time of Cooling and Flakes Found in Specimens from Six Heats of Steel

Cooling at Different Rates			Out at Different Temperatures			In at Different Temperatures		
Specimen No.	Number of Flakes	Time from Hr. Min.	Specimen No.	Number of Flakes	Time Hr. Min.	Specimen No.	Number of Flakes	Time Hr. Min.



Cent. ...minated ...al Size.

Table II

Method and Time of Cooling and Flakes Found in Specimens from Six Heats of Steel

Cooling at Different Rates			Out at Different Temperatures			In at Different Temperatures		
Specimen No.	Number of Flakes	Time from 900 to 200° F. Hr. Min.	Specimen No.	Number of Flakes	Time Hr. Min.	Specimen No.	Number of Flakes	Time Hr. Min.
				In 900° F.—Out 800° F.			In 500° F.—Out 200° F.	
2-6-0	10 L,	1 : 02	2-6-5	7 L,	: 12	2-6-9	0	18 : 54
2-6-1	2 L,	1 : 58	4-1-6	43 L, 7 T	: 22	4-1-9	0	18 : 55
2-6-2	0	3 : 46	6-2-6	10 L, 4 T	: 31	6-2-9	0	20 : 50
2-6-3	0	5 : 26		Hydrogen Treated Ingots			Hydrogen Treated Ingots	
2-6-4	0	9 : 30	3-2-5	280 L, 42 T	: 21	3-2-9	0	17 : 57
4-1-0	25 L, 1 T	: 53	8-2-5	29 L, 10 T	: 30	8-2-9	0	17 : 24
4-1-1	21 L, 4 T	1 : 13	12-3-5	20 L, 65 T	: 21	12-3-9	0	20 : 51
4-1-2	4 L,	1 : 48		In 900° F.—Out 700° F.			In 400° F.—Out 200° F.	
4-1-3	0	3 : 20	2-6-6	6 L,	: 36	2-6-10	0	12 : 36
4-1-4	0	5 : 47	4-1-5	7 L, 6 T	1 : 04	4-1-10	0	14 : 42
6-2-0	8 L, 9 T	1 : 02	6-2-7	0	1 : 17	6-2-10	0	14 : 48
6-2-1	13 L, 3 T	1 : 28		Hydrogen Treated Ingots			Hydrogen Treated Ingots	
6-2-2	1 L,	2 : 49	3-2-7	264 L, 46 T	1 : 08	3-2-10	0	11 : 36
6-2-3	0	5 : 26	8-2-6	8 L, 2 T	1 : 16	8-2-10	0	11 : 51
6-2-4	0	9 : 02	12-3-7	7 L, 24 T	: 59	12-3-10	0	18 : 27
	Hydrogen Treated Ingots			In 900° F.—Out 600° F.			In 300° F.—Out 200° F.	
3-2-0	167 L, 33 T	: 59	2-6-7	0	2 : 11	2-6-11	0	7 : 36
3-2-1	100 L, 14 T	2 : 07	4-1-7	0	3 : 14	4-1-11	0	5 : 24
3-2-2	63 L, 4 T	3 : 56	6-2-5	0	3 : 21	6-2-11	0	8 : 41
3-2-3	9 L,	6 : 38		Hydrogen Treated Ingots			Hydrogen Treated Ingots	
3-2-4	0	9 : 11	3-2-8	65 L, 14 T	2 : 29	3-2-11	8 L,	6 : 27
8-2-0	40 L, 6 T	: 59	8-2-7	2 L,	2 : 11	8-2-11	0	8 : 29
8-2-1	21 L, 5 T	1 : 32	12-3-6	0	2 : 55	12-3-11	0	7 : 57
8-2-2	3 L,	2 : 35		In 900° F.—Out 500° F.			In 200° F.—Out 100° F.	
8-2-3	0	4 : 00	2-6-8	0	4 : 35	2-6-12	0	18 : 03
8-2-4	0	5 : 44	4-1-8	0	5 : 20	4-1-12	7 L,	14 : 51
12-3-0	18 L, 94 T	1 : 13	6-2-8	0	6 : 41	6-2-12	7 L,	19 : 47
12-3-1	10 L, 40 T	1 : 59		Hydrogen Treated Ingots			Hydrogen Treated Ingots	
12-3-2	4 L, 2 T	3 : 28	3-2-6	0	6 : 04	3-2-12	104 L, 4 T	15 : 04
12-3-3	0	6 : 11	8-2-8	0	4 : 35	8-2-12	5 L,	21 : 00
12-3-4	0	10 : 05	12-3-8	0	7 : 08	12-3-12	1 L,	21 : 00

Conclusions

1. Judging from the vast amount of information in the literature and the results of these tests it can be safely concluded that hydrogen plays an important part in the development of flakes in steel.

2. The source of the hydrogen in steel and the mechanism of the formation of flakes were discussed in a previous paper (2) and two years additional work have not changed the writers' previously expressed opinions.

3. The amount of time required in slow cooling between 900 and 200 degrees Fahr. (480 and 95 degrees Cent.) to eliminate flakes in the type of bars used in this experiment (heaviest cross section 1½ x 3 inches, average 0.70 per cent carbon, 0.74 per cent manganese) varies from three hours, 20 minutes to nine hours, 11 minutes, depending on the tendency of the steel to develop flakes. This time required for slow cooling would not necessarily apply to bars of other dimensions or analyses.

4. Flakes developed in most of the above-mentioned bars below 300 degrees Fahr. (150 degrees Cent.) but in one test the flakes developed above this temperature. The temperature at which flakes form will probably vary with the tendency of the steel to develop flakes.

Acknowledgments

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DISCUSSION

Written Discussion: By I. C. Mackie, engineer of tests, Dominion Steel and Coal Co., Sydney, Nova Scotia.

As an interested observer of the work described in the paper by Messrs. Cramer and Bast I would like to submit a few comments. The "bars" referred to in the paper were in reality steel rails of 100-pound section and the flakes the defect more commonly known in rail mill parlance as shatter cracks. The work was done as part of an investigation which, it is hoped, will ultimately permit the drafting of an improved specification covering the controlled cooling of rails which practice is now in use in several rail mills. The present practice is entirely satisfactory in accomplishing the complete prevention of shatter. The possible improvement would consist in proving definitely that the time consumed in the retarded cooling as now practiced could be materially shortened without danger of producing rails containing shatter.

Although I have no doubt the authors and others who are responsible for the present investigation are fully aware of the practical difficulties in arriving at any perfectly safe answer to the problem, it seems an opportune time to give expression to a few facts which may emphasize the need for caution before drawing any final conclusions.

A successful process for the retarded cooling of rails was developed at the Sydney plant of the Dominion Steel and Coal Corporation and was in commercial use in the latter part of 1931. In the preliminary work leading up to the adoption of the process a large number of rail samples were examined for shatter after various retarded cooling treatments. It may be definitely stated that the prevention of shatter requires more time or slower cooling in the case of heavy rail sections than would be necessary with lighter rails. Tests on 100-pound rails can never be a safe guide to a general specification. It was presumably impatience to get on with the investigation that led to carrying out the tests at the Sydney rail mill without waiting for a rolling of 130-pound rails, more typical of the heavier sections in general use. The use of hydrogen treatment of the molten steel in the ingot mold to assure presence of shatter in naturally cooled rails will be discussed briefly later. Dealing for the moment with what we may call natural shatter as distinguished from what we may call artificial shatter resulting from hydrogen treatment, I have had an opportunity to examine results of retarded cooling experiments made by the same investigators at the rail mill at Ensley, Alabama, where the work was done on 130-pound rail sections containing natural shatter only. The conclusions that might seem justifiable from the Ensley experiments as to permissible range of temperature and rate of cooling to prevent the occurrence of shatter are not in agreement with numerous experimental results carried out at Sydney on 130-pound sections during the development of the retarded cooling process. The Ensley tests would indicate a more rapid permissible cooling rate than would be safe in the light of tests made at Sydney seven or eight years ago. The difference may arise from variations in the degree of shatter found in naturally cooled rails. A cooling treatment that may be quite safe for a rail with only slight or moderate tendency to develop shatter may be entirely in-

adequate for a rail that develops severe shatter on natural cooling. Any specification covering rail cooling should of course be safe for the worst cases and the heaviest sections.

Again in the commercial practice of retarded cooling of rails, the usual procedure is to stow the hot rails in a number of tiers in large box-like enclosures, each tier consisting of perhaps ten, twelve or more rails. In one box there may be as many as 200 rails. Usually a thermocouple is installed approximately in the center of the cross section of the rail pile and extending some feet in from the ends of the rails. The cooling rate of the pile is determined from the indications of such a location. Naturally in such a pile of rails there is wide variation in the cooling rate of individual rails. The fastest cooling rail will generally be the outside rail in the bottom tier. In commercial practice it would not be easy to determine the exact cooling rate of the end portion of this most rapidly cooling rail in the pile. The present investigation, dealing as it does with well insulated single pieces of rail, may, after a great many tests, during which we may hope rails will be encountered of the heaviest section and of the maximum tendency to develop shatter, arrive at the cooling rate and temperature range for retardation that will safely prevent shatter. To pass from the conclusions of such a test to the fixing of a cooling rate for a commercial pile of rails whose temperature is taken in the manner above described is a problem in itself, and would be complicated by the variations in degree of protection afforded by the rail enclosures at various mills, more particularly as they affect the cooling rate of the most rapidly cooling rail in the pile. Such an investigation as the present one, if it is to be based on natural shatter only, would not be safely concluded at the present rate by years of work. So often, as we found in the early work at Sydney, experiments that were hoped would give important information were rendered useless by the entire absence of shatter in the naturally cooled rails, or by a very mild occurrence of the trouble.

This brings us naturally to the question of the legitimacy, shall we call it, of artificially insuring comparatively severe shatter in naturally cooled rails by hydrogen treatment, so that the investigation may proceed in a reasonable time to some conclusion as to what cooling treatment will be adequate. Here we can give only opinions, for no one is yet in a position to say that hydrogen is the sole cause of shatter as found in commercial rails cooled naturally on the mill hot beds. I am glad of this opportunity to express an opinion on this matter. Before doing so it may be of interest to state that we have at Sydney occasionally encountered natural shatter fully as severe or more so, on naturally cooled rails, than shown by the specimens of hydrogen treated steel described in Messrs. Cramer and Bast's paper under the serial number 3.

In the earliest stages of development at Sydney of a rail-cooling process for the prevention of shatter we naturally worked on the theory that shatter was caused by stresses set up within the rail head by temperature differences. We had not gone very far when this theory became wholly untenable. On any one day the cooling conditions on the mill hot bed would not differ appreciably and yet some heats of steel would be entirely free from shatter and others show it decidedly on every rail examined. It was not very long after the commercial development of the process that the opinion was formed that the

essential cause of shatter was a gas, and probably hydrogen. This idea was really more than just a hunch, to use a popular expression, but it would take too long to give the various reasons that led to this opinion. As a matter of fact in January 1935 a number of officials from one of the American rail plants visited Sydney and in the discussions one of the visitors asked what we considered was the real cause of shatter. The answer was hydrogen. It was some months later that the first German publications appeared with definite evidence that hydrogen could cause flakes in steel.

When Mr. Cramer, before coming to Sydney for the work described in the paper under discussion, asked if we would agree to the hydrogen treatment we were very glad indeed to consent, knowing how likely the experiments were to be abortive unless decided shatter could be obtained in naturally cooled rails. The first ingot treated with hydrogen by Mr. Cramer and his associates was I believe the one described in the paper under the serial number 3, the worst specimen encountered. A test piece had been rushed from the hot saw to the laboratory for deep etch tests and was found very badly shattered. The rail mill superintendent telephoned to ask whether the rails from the hydrogen treated ingot should be allowed to go along with the rest of the heat into the slow cooling boxes. Actually it never occurred to me to say anything but "certainly." These rails were spotted in the box and later tests showed that the regular retarded cooling process had entirely prevented shatter in these rails.

As before stated we are dealing here with opinions only and no more need be said to indicate that the writer is convinced of the legitimacy of the hydrogen treatment as a useful procedure to insure severe shatter in the rails used for retarded cooling experiments.

I note that Mr. Ashdown, in discussing the paper submitted by Mr. Cramer at the 1936 meeting of the Society, could not agree with the hydrogen theory of flake formation. From his discussion at that time I quote the following:

> "It is now well known that flakes existing in steel billets will weld up on reforging but, if the billets are again cooled in air to normal temperature, a fresh crop of flakes, usually smaller, will develop."

What may be the facts in the case of alloy steels, I do not know. Our experience with rail steel is certainly not in agreement with the above quotation.

Furthermore any trials we have made indicate that a rail, prevented from shattering by a retarded cooling process, can then be reheated to rolling temperature and allowed to cool naturally in the air without showing a trace of shatter, although naturally cooled rails as first rolled from the same heat may show bad shatter cracks. The same result has, I believe, been obtained by other mills and other investigations.

Written Discussion: By Gilbert Soler, manager of research, and Weston Hare, research engineer, Steel and Tube Division, Timken Roller Bearing Co., Canton, O.

The work of Messrs. Cramer and Bast is of considerable interest in giving further evidence of the nature and cause of flakes in steel. Their work is particularly pertinent since they have worked with production size samples in treating large ingots to determine the effect of cooling rates and hydrogen content on flaking of rolled bars. The conclusion seems reasonable that hydrogen is the primary cause for flake formation. The exact mechanism is

probably not yet proven, however, as the question remains as to the effect of the hydrogen addition on the physical properties of the steel; that is, on the manner of crystallization, grain size, distribution of nonmetallic inclusions and possible hydrogen embrittlement.

It would be interesting to have the authors' idea as to the nature of the voids in which the hydrogen collects. Many references in the literature state that the voids are microscopic in size and are possibly around inclusions in the steel. In our work we have noticed the presence of tubular voids in longitudinally fractured pieces of flaked steel. These tubular voids are several thousandths inch in diameter and up to ¼ inch in length, and were undoubtedly filled with gas under pressure, probably hydrogen. The assumption seems warranted that gas was present in the ingot as bubbles trapped during freezing, and these bubbles were drawn out into tubes during rolling.

It is interesting to note the statement that when the flakes are large, they are relatively few, and when small are more numerous. Possibly the large flakes are connected with coarse primary dendrites and small flakes with finer primary crystals. It seems that this assumption would also explain the tendency noted in Fig. 5 and Table II of Cramer and Bast's paper that coarse flakes seem to tend toward a transverse direction. There must be some unusual transverse weakness to overcome the usual higher transverse properties of rolled bars.

It is somewhat unfortunate that Messrs. Cramer and Bast found it necessary to use ingots from different heats for the control tests and the hydrogen treated tests. It would have been interesting to note the effect of hydrogen on an ingot as compared with an adjacent untreated ingot.

Although we have analyzed the hydrogen content at tapping time of many heats in our plant, we have never correlated the analyzed hydrogen content of heats with their respective tendency to burst, although such a study would be of interest. However, many other factors than actual hydrogen content before teeming may affect the amount of gas retained in the solid steel such as rate of pouring, rate of solidification, and the extent of nuclei for gas evolution.

In regard to cooling rates for the prevention of bursts it is interesting to note that slow cooling from 900 to 500 degrees Fahr. in 6 hours will prevent bursts as well as slow cooling from 400 to 200 degrees Fahr. in 12 hours. This is illustrated in Fig. 3 by specimen 3-2-6 and specimen 3-2-10, as well as the data for all heats in Table II. While this relation probably holds only for the bars of the dimensions and analysis used in the experiment it is of practical significance. The location of the cooling pits or tanks in respect to the location of the cooling bed and the time required to move steel from the cooling bed to the pits may determine whether cooling can be done most advantageously in the upper range (900 to 500 degrees Fahr.) or in the lower range (400 to 200 degrees Fahr.). It might also be desirable to cool in a given range to prevent bursts and at the same time control hot-rolled properties such as hardness, cold shear quality, warping, etc.

Written Discussion: By H. B. Wishart, metallurgist, Carnegie-Illinois Steel Corp., Gary, Ind.

Messrs. Cramer and Bast have very ably reviewed in a brief manner recent literature and have given an extensive bibliography in their paper on

the problem of flakes or shatter cracks in steel which is helpful in the study of this subject.

As the authors mentioned, there has been and still is a controversy over the cause of flakes in steel. There are some investigators who feel that cooling stresses are responsible for their formation while other investigators feel that a combination of cooling stresses and stresses created by gases are the cause. It is evident if cooling stresses alone were responsible for flakes or shatter cracks, taking railroad rails as an example, they would occur in the entire output of rails if hot bed cooled. Such an occurrence is not the case because the percentage of hot bed cooled rails containing shatter cracks is very small. As the method of cooling this product follows a uniform practice there must be some other cause that occasionally augments the cooling stresses to such an extent that internal damage occurs in the rails—that this cause could be gases, especially hydrogen, has been shown in this paper. The exact mechanism by which the gases produce failure is not definitely known although it is fairly well established that flakes do not tend to form in a flake sensitive steel until a temperature in the neighborhood of 400 degrees Fahr. is reached.

Several methods are now in use to prevent flake formation in steel, one of which is the controlled or retarded cooling of the finished product as mentioned in this paper. Another method of preventing flakes in steel was recently devised by A. N. Swanson[1] and the writer and seems to substantiate the gas theory of flake formation. The method briefly consists in allowing the metal to cool in air after the last hot working operation to any given temperature within the range of 500 degrees Fahr. and the critical temperature. The cooling of the steel is to be retarded and held at a temperature selected in this range for a given period of time depending on the mass of the metal and then allowed to cool in air. It was found that the higher holding temperatures, 1000 to 1200 degrees Fahr., were the most effective temperatures in eliminating the flake sensitivity of the steel.

The problem of flakes in steel is not a new one. Many attempts have been made to find the source of trouble in the steel in the various stages of its manufacture but it was not until recently that the apparent cause of the trouble was discovered and methods devised to prevent flake formation. The authors are to be commended on their contribution to the field of flake prevention which shows that gases can cause flakes, and some of the various methods of controlled or retarded cooling that will prevent flakes.

Oral Discussion

H. W. McQuaid:[2] Anyone who has had much to do with melting steel has seen the results of hydrogen. I can remember in making electric furnace steel of the low carbon carburizing grade from baled turnings that we had great difficulty in keeping it from going wild in the molds. The steel would lie quietly in the molds for 5 or 10 minutes and then would start to rise, and in a few minutes most of the steel would be on the outside of the mold. The difficulty was traced back to oily scrap or leaky cooling rings on the carbon

[1]Assistant chief metallurgist, Gary Works, Carnegie-Illinois Steel Corp., Gary, Ind.
[2]Assistant chief metallurgist, Republic Steel Corporation, Cleveland.

electrodes. Apparently the hydrogen in solution would be unusually high in these heats and would keep coming out of solution while the steel was still in the mushy stage so that the expansion of the trapped hydrogen would be sufficient to cause the wildness in the mold. Similar difficulties can be traced to wet limestone, wet hot tops and wet stool brick. Some furnaces which are fired with steam atomization of the fuel occasionally have the same difficulty.

About 20 years ago a paper was given by Styri, in which he connected the cause of wildness, etc., in ingots to atmospheric conditions, and I have noticed in steel castings that there is an increase in the amount of porosity during warm humid weather. Whether hydrogen caused this I do not know, but I do believe while it is a contributing factor in the formation of flakes it is hard to prove that it is the primary cause. I do not know whether the observation that moisture is the cause of porosity in castings is universal in its application, but it has been made often enough to indicate that hydrogen is an important factor in the soundness of the castings, whether it be a commercial casting or an ingot.

JOHN CHIPMAN:[3] I would like to remark that this is a very beautiful piece of work and quite different from the older work that was reported on gases in metals some 10 or 20 years ago, in which almost everything that could go wrong with the metal was blamed on gas. Here we have some very definite, tangible evidence of a perfectly well recognized effect of hydrogen gas. This is finally something upon which one can place his finger and say here is an effect of the hydrogen.

F. B. FOLEY:[4] The name "flake" as applied to the type of defect discussed in this paper by Cramer and Bast is a contraction of the word "snow-flake" used during the war period of 1917-18 to describe the appearance of a defect found in tensile test specimens and ordinary fractures from certain nickel steel gun forgings. Such fractures contained bright areas such as might be produced by pressing a small piece of thin silver foil onto the fracture. Tensile test bars found to contain these defects developed full tensile strength and elastic limit, but were characterized by low elongation and reduction of area. Another type of defect, which undoubtedly was a thermal crack and produced by too rapid cooling immediately following the forging, had a different appearance, being very coarse where the crack existed, and gave results in tensile tests which were low in every respect. It is this latter type of defect with which I believe the authors are at present concerned and which are aggravated by the presence of hydrogen and readily developed by too rapid cooling following hot working.

It is characteristic of cooling cracks that they are confined to the deep-seated layers of metal and do not occur near the surface nor close to the ends of bars or forgings, yet it is well known that, in spite of the fact that they are rarely if ever found in the portions of the metal where cooling is most rapid, rapid cooling develops them and slow cooling after forging or rolling prevents their occurrence. It was my observation of thermal cracks which I examined during the war period that they were generally associated with a coarse austenitic grain size in the forging.

[3]Department of metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.
[4]Superintendent of research, The Midvale Company, Nicetown, Philadelphia.

Another fact which seems to run counter to the general idea that it is wholly the cooling rate which causes cooling cracks is that they rarely if ever occur in small sections, under say 2½ inches square, which cool more rapidly than the larger sizes. Of course it can be said that the requisite stresses are not present in the small sections.

It is my experience that once a steel, subject to thermal cracking during cooling, has been cooled from the forge or mill in such a manner as to avoid their presence it may then be reheated to a normalizing temperature and cooled in air, a rate which if applied to the piece as it comes off the mill or hammer would cause cracks to develop, without developing any cracks. Hultgren found that chromium-bearing steel finished at a low temperature in hot working was generally free of cooling cracks, although the same steel finished hot readily developed them.

Alloy steels, when made in an acid furnace, are much less likely to develop thermal cracks than a similar steel made by the basic process.

C. E. Sims:[5] After the authors' presentation there can be very little doubt as to the cause of this trouble, but there does seem to be some question as yet as to just what the mechanism is. I would like to cite a few experiences which I have had in cast steel which has an analogous condition and which is most certainly due to hydrogen.

We find in normalized test bars, that is, normalized as 1-inch sections, after breaking in a tensile machine, certain little spots usually about $\frac{1}{64}$ of an inch to as big as $\frac{1}{32}$ of an inch in diameter. When the bar is broken the fracture will usually zigzag back and forth through those spots resulting in a very jagged fracture. At these peaks and valleys you will find an irregular spot usually fairly round and in the center of which there will be a very tiny cavity. This spot will have a very fine-grained fracture like a hard, brittle steel, very much like a high carbon steel, whereas the rest of the area will have a fibrous appearance. This brittle area is always concentric with the small cavity.

Now, if we should age that bar at some low temperature, even at room temperature if it is aged long enough, and then break it, the spots will not appear. This is evidence that there are no fissures or cracks prior to breaking the bar and this condition is due to the manner in which the steel fractures. At room temperature it may require two or three weeks but if we age it at 200 or 300 degrees for about 15 hours the spots will disappear. At temperatures of 500 to 700 degrees the condition is cured in a very few hours. A peculiar thing about it is that, if the bar is renormalized after aging to remove the spots and then pulled without reaging, the spots would reappear. This condition in cast steel has been known and worried about for a good many years. Although hydrogen had been suspected, the first definite indication was obtained when we broke some welded bars that had been welded with atomic hydrogen. Of course, the weld metal all solidified in an atmosphere of practically pure hydrogen and we found the same condition but in a greatly exaggerated state. Instead of spots $\frac{1}{64}$ inch in diameter there were spots ⅛ inch

[5]Research metallurgist, Battelle Memorial Institute, Columbus, O.

in diameter with the same typical hole in the center. These spots could also be eliminated by low temperature aging.

I will give briefly some more or less tentative conclusions that seem to fit the facts in the case. First is that hydrogen is soluble in liquid steel and when there is too much or if there is sufficient FeO there will be a gaseous effervescence during freezing. In other cases there will be no effervescence but the hydrogen seems to segregate nevertheless and tiny interdendritic cavities will be filled with hydrogen.

Another thing is that hydrogen apparently forms a stable hydride at high temperatures with steel. This hydride is unstable at low temperatures but, owing to the sluggishness of the steel, the decomposition of the hydride is extremely slow. Slightly elevating the temperature will hasten the decomposition of the hydride. We have an analogous condition in electrolytic iron, fresh cathodes of which are brittle as antimony but which when heated up become almost as soft as tin.

This condition described as occurring in cast steel is apparently analogous to the occurrence of flakes in rolled and forged steels. If there were only longitudinal flakes in rolled steel they might be attributed to rolled out gas filled cavities but there are just as many transverse as longitudinal flakes.

H. W. McQuaid: It seems to me that we ought to go a little slow in saying that hydrogen is the direct cause of flakes. About ten years ago in the British Iron and Steel Institute, out of many discussers of Mr. Hultgren's paper on flakes, there was, I think, only one metallurgist who disagreed with the conclusion that flakes were caused by thermal stresses. The rest of them were absolutely certain the cause of flakes in steel was too fast cooling of the bloom. They said that it was very obvious the cause of flakes was too fast cooling. Now the consensus of opinion seems to be that flaking is due to hydrogen absorbed in melting and the one English metallurgist was correct.

It seems to me we should be careful about jumping at conclusions in such matters and that the effect that we get which shows up as flakes may not necessarily be due directly to hydrogen but to the hydrogen effect. This effect may be on carbide diffusion rates, inclusion types, or on reaction to cooling. If hydrogen is so important in commercial steel it seems to me that in making test heats and special heats in which we place great stress on the result of experimental demonstration of certain factors that it is a little bit foolish to remelt or make the final melting in a hydrogen atmosphere and say the hydrogen has no effect upon the results produced. I think it has been well demonstrated that hydrogen has a direct effect upon the results obtained on cooling and the stresses set up in fast cooling.

Judging from what Mr. Foley said, sensitivity comes from the casting condition, and in the bloom the cast structure has not been broken up very well. I know very well from experience that if you can break up the cast structure and cool down without flakes that you never see them again.

Mr. Sims mentioned conditions which are quite common with flaked steel showing up in tensile tests. The interesting thing which I have observed where you have flaked tensile test is that the effect of flakes on ultimate strength seems very little, whereas the effect on the elastic limit is very marked. I can recall a badly flaked Cr-Ni-Mo steel which would show approximately 200,000

pounds per square inch ultimate strength whereas the elastic limit would be less than 100,000 pounds per square inch. In the nonflaked material the elastic limit would be close to 160,000 pounds per square inch.

AXEL HULTGREN:[8] When I published some work on this subject in 1925 I was dealing with ball bearing chromium steel only. Since then I have had occasion to examine chromium-nickel-molybdenum steel; one heat that was particularly sensitive to forming these flakes was selected for the experiments. Twelve inch square bars were forged. After ordinary forging followed by slow cooling in charcoal dust, the main central portion of the bars contained numerous cracks. My working hypothesis was as follows: In forging you cool the outer layers of the steel. When you finish forging you have only small residual forging stresses but a nonuniform temperature distribution of the kind that will cause the formation of additional tensile stress in the center at a later stage when the temperature becomes equalized. So that, I think, may throw some light on Mr. Foley's observation regarding reheating and normalizing a cold bar and not finding any cracks. In that case you do not have the same initial condition when you cool.

Now in order to test this idea I took the forged bars and reheated them immediately to a series of temperatures: 1652, 1832, 2012, 2192 degrees Fahr. (900, 1000, 1100, 1200 degrees Cent.) and kept them at temperature for different periods. After annealing at 1652 degrees Fahr. (900 degrees Cent.) for 3 hours followed by air cooling there were numerous cracks; 1832 degrees Fahr. (1000 degrees Cent.) for one hour, air cooling: no cracks; 2012 degrees Fahr. (1100 degrees Cent.) the same; 2192 degrees Fahr. (1200 degrees Cent.) a few cracks were formed at the corners which were probably caused by the cooling stresses. Anyhow, the results seemed to bear out the idea that the stresses were the main cause of the flakes and that holding the forged bar at a sufficiently high temperature so as to equalize its temperature and also the stresses produced in equalizing would be beneficial. Afterwards, of course, the well-known extensive work at the Krupp Works has been done and called our attention to the effect of hydrogen. I am convinced that this work which has also been confirmed in this paper of today points to a real effect of hydrogen but I am not so convinced that stresses in practice do not also play a dominant part in the production of the flakes. The main thing now, in my opinion, is to study the conditions in practice: the possible origin of hydrogen and the possible origin of stresses that may combine to form these cracks.

Just another word on the subject of Mr. Sims' discussion. I have also seen similar fracture phenomena in weld material obtained from electrodes having a coating that gave off gas and had a reducing character. It should be pointed out that these cracks or spots that are visible in the fracture around the blowholes are formed in the tensile test. They are at right angles to the direction of pull. A snow flake, on the other hand, is a crack that is there before you deform the steel. It is just as easy or difficult to explain a longitudinal as a transverse snow flake. The shape of the snow flake is very seldom elongated. It is not present during forging but is formed during the subsequent cooling.

[8]Professor of metallography, Tekniska Högskolan, Stockholm, Sweden.

H. D. PHILLIPS:[7] In reference to the condition which Mr. Sims described here in certain cast steels, we have found that in making acid electric steels that, if the metal is prepared in such a way that you do not get a good "boil" and you then add aluminum to it and get a thorough deoxidation, you are quite likely to develop that condition which Mr. Sims has illustrated. However, even if you do "boil" the steel but add no aluminum to it and cast it in green sand, you are quite likely to get porosity and that probably is due to hydrogen. At least that has been the experience of most foundry men. If you add just enough aluminum to thoroughly deoxidize, even with a properly made steel you would get a network sulphide structure but little evidence of these flaws.

I am not going to get into the argument of just what it is, but that is the condition that we run into. If you add an excess of aluminum and cast it in green sand, you are quite likely to develop these spots in the tensile bar if the steel has not been properly made.

The mold condition has a lot to do with it also. If you make a casting six or eight feet long in green sand with a high moisture content and take one test bar at the gate end of the casting and another test bar at the far end of the casting, the one at the far end is quite likely to have these spots whereas the one at the gate end does not have them. That seems to indicate hydrogen. In foundry practice when we find a condition of that sort we invariably get a cure for it by aging at 500 to 700 degrees Fahr. In castings we find an increased susceptibility toward this condition when our steel is deoxidized by large additions of aluminum.

H. W. MCQUAID: It always has seemed to me the difference in size between 19 and 24-inch steel ingots and ordinary steel casting is sufficient to explain the greater tendency of the steel in ingot form to show the flaked condition than steel castings. In steel castings flakes are very scarce compared to what you get from ingots in normal steel practice.

Authors' Reply

We wish to express our appreciation for the written and oral discussion of this paper.

We heartily agree with Mr. Mackie that due precautions must be taken in drawing conclusions from our work or making recommendations of changes in the commercial practice of slow cooling because of some differences in conditions between our tests and commercial practice. Mr. Mackie speaks from years of experience on this problem and we have high respect for his opinions.

The written discussion of Messrs. Soler and Hare suggests several questions which are unanswered regarding the effect of the hydrogen on the physical properties of the steel, on the manner of crystallization, grain size, distribution of nonmetallic inclusions and possible hydrogen embrittlement. So far we have made only a comparatively few microscopic examinations of hydrogen-treated bars and have not noticed an appreciable difference between them and untreated bars. We have not found the tubular voids they mention but will search for them more thoroughly. We have in mind, as the space where hydro-

[7]Dodge Steel Company, Tacony, Philadelphia.

gen may collect, any lack of contact or weakness between inclusions and steel which might result from unequal shrinkage during cooling.

We believe the relation between size of flakes and number of flakes is somewhat like grain size; that is, in a given volume of steel if the number of either is large the size will be small and vice versa. This brings up the question whether flakes form by a sudden break to full size or by a slow growth. It seemed logical to us to assume that if the concentration of hydrogen trying to escape from the steel is high it builds up enough pressure to start fracturing the metal at a large number of locations, let us assume them to be ¼ inch apart throughout the metal. Then because of the closeness of these nuclei the amount of hydrogen which will diffuse to each crack will be limited, therefore the size of the flakes will be small. If, however, the cracks start at centers 1 inch apart the hydrogen from a larger volume of metal may diffuse to each crack and they will grow to a larger size. This explanation indicates that the cracks may develop slowly as more hydrogen diffuses into them.

In answer to Messrs. Soler and Hare's question of the comparison of bars from the hydrogen-treated ingots and bars from an adjacent ingot, we should have included in the paper that we did obtain test pieces from an ingot adjacent to two of the hydrogen-treated ingots and both were free of flakes. Since this paper was written, we have repeated this experiment at another steel mill and obtained this same result. That is, bars from the hydrogen-treated ingots developed from 100 to 300 flakes while bars from an adjacent ingot were free of flakes. It was an oversight on our part that we left this information out of the paper.

The observation was made by Messrs. Soler and Hare that 6 hours of cooling between 900 and 500 degrees Fahr. eliminated flakes while 12 hours were required when the slow cooling was done between 400 and 200 degrees Fahr. This point is covered more completely in the discussion submitted by Mr. Wishart in which he describes another method of preventing flakes in steel. He reports that holding the steel in the range of 1000 to 1200 degrees Fahr. as the most effective temperature to eliminate flakes. We consider this important information and appreciate Mr. Wishart presenting it in his discussion.

We are very glad to hear of Mr. McQuaid's experience with electric furnace steel and especially to hear his explanation of the sources of hydrogen in this type of steel. His experience with steel castings is equally interesting.

Dr. Chipman's comments are very encouraging to us coming from one who has directed so much research on gases in steel.

Mr. Foley's explanation of the use of the terms flake or snow flake to describe bright spots on the fracture of tensile specimens is new to us. We had thought these terms were only used to describe the bright spots found on the fractures of heavy sections, the second type described by Mr. Foley. We are familiar with the first type of bright spots he describes and have found that in some cases they are due to early interior fractures of the tensile specimens developing around inclusions. The area which fractures first is not deformed as the tensile specimen necks down and therefore appears bright in contrast to the surrounding material in which the crystals were deformed

during the necking of the specimen, producing a dull, fibrous appearance after fracture. The presence of inclusions in the center of the bright spots was proven by polishing the specimens longitudinally down to the center of the bright spots and examining them on the microscope.

We agree with Mr. Foley's observations that flakes do not occur near the surface or ends of bars or forgings and believe this is explained by the escape of hydrogen from the metal near the surfaces, which prevents the building up of high enough internal pressures to crack the steel. This also explains why bars of small sections, as under 2 inches square, do not develop flakes. It should also be considered that thermal stresses probably play some part in the development of flakes and these are lower near the surface of a large bar and at the interior of small bars in contrast to the thermal stresses developed at the interior of a large bar. As Mr. Foley states, flakes seldom develop except during the first time the steel is cooled to room temperature after being cast in the ingots. This made it necessary to conduct our experiments at the steel mill on bars rolled directly from the ingots. Flakes do not often develop in bars rolled from reheated blooms.

Mr. Sims presents a very unusual problem which is rather puzzling to us. Most of the observations he describes are entirely in accord with the theory that hydrogen could be the cause of his troubles. However, his specimens have been cooled to room temperature several times which should allow the hydrogen to escape from a 1-inch round steel bar. We would be inclined to investigate the presence of inclusions, which may drop out and be unnoticed, as playing some part in this problem, although the inclusion idea does not explain how aging could eliminate the trouble.

In Mr. McQuaid's third discussion he mentions tensile specimens which show flakes on the fracture but have high ultimate strengths. We think a clear distinction should be made between the bright spots observed on tensile specimens and flakes present in large steel bars. It should be recognized that these bright spots develop during the fracture of the tensile specimen and were not present before the tensile test. We have occasionally made tensile tests of specimens machined from flaked steel and in this case it is unusual to obtain one-half the ultimate strength which would be obtained on a specimen not containing flakes.

Professor Hultgren's experience with 12-inch forged bars of chromium-nickel-molybdenum steel certainly emphasizes the fact that no one should jump at the conclusion that hydrogen is the only cause of flakes. As we follow his description of this experiment we cannot see why all the bars should not have developed flakes and hydrogen been the chief cause of the flakes developed in the bar heated to 1652 degrees Fahr. (900 degrees Cent.) and cooled in air. In this connection we have information that hydrogen-treated steel held above the critical range does not lose its hydrogen very fast but when cooled below the critical range a large part of the hydrogen diffuses out rather rapidly.

SOME PROPERTIES OF OXYGEN-FREE HIGH CONDUCTIVITY COPPER (OFHC)

By Claus G. Goetzel

Abstract

Test specimens for density, hardness, tension, compression, impact, fatigue, electrical conductivity, and structure tests were prepared from two small OFHC castings. Tension, conductivity, and fatigue tests were made on as-cast material and on wires, rolled and drawn from bars cut from the castings. Density, hardness and structure tests were made on as-cast OFHC and on samples which have been compressed in a steel die after separation from the casting.

Tension tests showed uniform results, independent from the location of the specimens in the casting. Compressive strength properties were uniform; odd shapes of the specimens after testing were traced back to the location of the cylinders in the original casting.

The influence of the die compression was very slight with respect to density, but marked with respect to hardness. The hardness values, however, did not reach heights of strain hardened copper. The die compression did not affect the macrostructure.

Conductivity tests gave slightly higher results than expected. They showed a considerable increase after annealing of the wires.

Impact tests had inconsistent results and showed the influence of the location of the test bars in the original casting.

Fatigue tests on as-cast material resulted in a S-N curve much lower than the one known for hard drawn solid OFHC, whereas the curve for hard drawn OFHC wires is only slightly below the curve for hard drawn solid material.

DURING an investigation on synthetic copper powder compacts it was found necessary to establish comparison data on cast copper under exactly the same testing conditions. Oxygen-free high conductivity copper (OFHC) was chosen as the most suitable cast

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copper as means of comparison, due to the well known outstanding results of previous investigations on this particular type of material.

Webster, Christie and Pratt[1] compared the tensile properties of OFHC copper with tough-pitch and with phosphorized ordinary copper in the annealed and in the cold hard drawn condition. They found some notable improvements in the properties of the OFHC type.

Rolle and Brace[2] made an intensive investigation on the properties of OFHC copper and also dealt with its use. In a series of photographs they showed the typical cast structure with its columnar grains. They also presented a set of photomicrographs of wirebars and wires of the different types of material, showing the deoxidized structure of the OFHC metal. The authors dealt further on with the tensile properties and endurance qualities of the material. The effect of cold working on the endurance limit of OFHC copper was studied. The endurance of OFHC under severe bending was compared with copper of the commercial types. Fatigue tests were run on OFHC hard drawn copper, having an ultimate tensile strength of 56,750 pounds per square inch. A Farmer-type rotating beam machine was used, and the values obtained were plotted in a S-N curve. However, no investigations were made on the as-cast material. Bending tests and twisting tests with OFHC and electrolytic tough-pitch copper showed OFHC to be considerably superior in its properties.

Lorig, Dahle and Roberts[3] recently investigated the mechanical properties of straight OFHC together with phosphorized OFHC and ordinary tough-pitch copper at elevated temperatures. Besides the values for the tensile properties some interesting results were obtained at room temperatures and at elevated temperatures with Charpy impact tests. The authors found that in the as-cast condition, the phosphorized OFHC copper was slightly superior to the other types of copper in tensile strength at elevated temperatures and was more ductile. After hot working and annealing, the straight OFHC copper was uniformly ductile, whereas the other types showed a marked decrease in ductility at higher temperatures. Impact strengths of straight and phosphorized OFHC coppers were superior

[1] "Comparative Properties of Oxygen-Free High Conductivity, Phosphorized and Tough-Pitch Coppers," by W. R. Webster, J. L. Christie, and R. S. Pratt, *Proceedings*, Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, 1933.

[2] "Oxygen-Free High Conductivity Copper: Its Properties and Uses," by S. Rolle and P. H. Brace, *Mining and Metallurgy*, August 1933.

[3] "The Mechanical Properties of Copper at Elevated Temperatures," by C. H. Lorig, F. B. Dahle, and D. A. Roberts, *Metals and Alloys*, March 1938.

to the impact strength of tough-pitch copper, but not much difference was observed in the as-cast impact properties of the straight and phosphorized OFHC coppers.

The purpose of this paper is to fill the little gaps, which the previous investigations left open; for instance, to establish fatigue data on as-cast OFHC and to investigate less important mechanical properties, such as Izod impact strength, compressive strength or fatigue properties of hard drawn wires, but also to give average values, suitable for comparison. Special attention is to be given to the location of the test specimens in the raw castings and also to the method of production of the test samples.

Material

Two small OFHC castings, approximately 2½ inches in diameter and 8 inches long, were received from the refinery of the United States Metals Refining Co. They were vertically cast at a temperature of 1130 to 1140 degrees Cent. (2065 to 2085 degrees Fahr.) in a water-cooled steel mold. The regular mold dressing of bone black was used. The raw material consisted of electrolytic copper cathodes analyzing 99.97 per cent plus copper.

Preparation of Test Specimens

The locations from which the specimens were taken are shown in Fig. 1. Each of the two ingots "A" and "B" yielded the same amount and the same types of test pieces.

The following list gives the specimens which each casting yielded:

Nos. I, II, Specimens for tensile tests
Nos. III, IV, Specimens for compression tests
Nos. V, VI, VII, VIII, Specimens for impact tests
Nos. IX, X, XI, XII, Specimens for conductivity and wire tests
Nos. XIII, XIV, Specimens for density and hardness tests
Nos. XV, XVI, XVII, XVIII, XIX, XX, XXI, XXII, Specimens for fatigue tests.

As Fig. 1 shows, the axes of the slugs for the density and hardness tests and of the cylinders for the compression tests were perpendicular to the axes of the castings, while the axes of all other specimens were parallel to the axes of the castings. The specimens were cut out of the ingots by sawing and milling operations and finished by machining and polishing.

The shape of the tensile specimens did not correspond to the American Society for Testing Materials standards with respect to their length. The sketch of Fig. 2 shows the size of the tensile bars. Their shape was governed by the size of the die available for the manufacture of the copper powder compacts of the main research work.

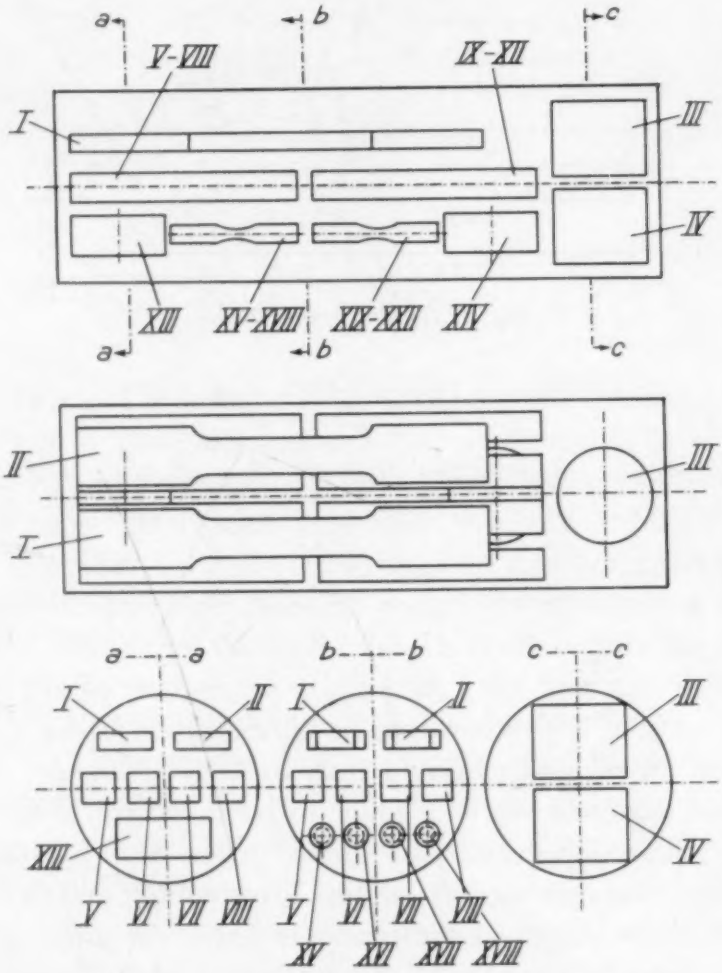


Fig. 1—Position of Test Specimens in Raw Casting.

The test cylinders for the compression tests corresponded to the American Society for Testing Materials specifications for the short specimen type. The diameter of the specimens was 1.13 inches, the length 1 inch. The ratio between length and diameter was approximately 0.9.

The size of the impact test specimens was chosen in accordance with the specifications for the Izod impact testing machine used. The cross section of the bars was 10 x 10 millimeters, the length 75 milli-

meters. Each specimen was provided with two notches of standardized size and shape. The first notch was machined at a distance of 25 millimeters from the one end, the other in a face, perpendicular to the first one, and at a distance of 25 millimeters from the other end of the bar.

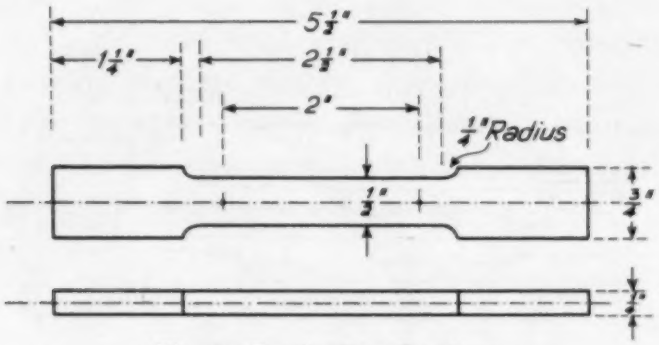


Fig. 2—Tensile Test Specimen.

The specimens for the electrical conductivity and wire tests were similar over-all dimensions, i.e., 3 inches long and with a cross sectional area of ⅜ x ⅜ inch. After testing of conductivity the bars were cold-rolled to a square cross section of 0.0055 square inch, i.e., the rolling reduction was 96.5 per cent. The wires were then drawn to 0.060 inch in diameter through a drawing plate with twelve orifices. The total drawing reduction was about 49 per cent. About one-third of each bar was used for such a production of wire by direct reduction, without any preheating or annealing, in order to show the extraordinary malleability and ductility of OFHC copper. The other part of each bar was worked down to wire according to the above procedure with one intermediate anneal after 41.5 per cent rolling reduction and one intermediate anneal after rolling and before drawing. Half of the length of the final wires was cut off and again annealed, the other half was used for testing as hard drawn. Annealing was done at a temperature of 550 to 600 degrees Cent. (1020 to 1110 degrees Fahr.) in a small electric muffle furnace for one hour in a slightly reducing atmosphere of CO and CO_2, produced by charcoal.

The slugs for density and hardness tests were 1.13 inches in diameter and ½ inch long. One slug per casting was strain hardened by compression at 45 tons per square inch when molded in a hardened steel die of the same diameter.

The specimens for the fatigue tests had a special size as required by the particular type of fatigue testing machine used. Fig. 3

shows a sketch of the fatigue specimen. The critical diameter was determined by the strength of the material tested, the magnitude of the computed stress, and the capacity of the machine. The critical diameters of the specimens were not the same and ranged from 0.16 to 0.20 inch. The specimens were polished after machining in order to assure uniformity of finish and freedom from annular scratches.

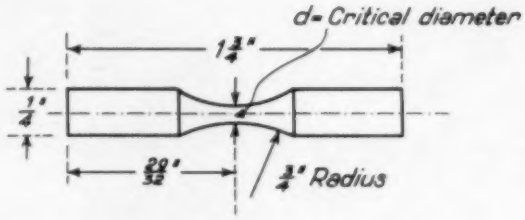


Fig. 3—High Speed Fatigue Test Specimen.

Testing Equipment and Procedure

The machine used for the tension tests on the solid material was a Southwark-Emery hydraulic tension machine of 20,000 pounds capacity. During the tension tests the yield point was only roughly checked by observation of yielding of the specimens by means of a caliper. The per cent elongation in 2 inches was recorded.

For the tension tests on the drawn wires a 1000-pound Amsler tension machine with pendulum weight adjustment was used. No yield point was determined. Wires with a gage length of 2 inches and also of 10 inches for both the hard drawn and the annealed types were tested for tensile strength and elongation. The gage length of 2 inches was used for comparison purposes with the powder materials of the main research work, the gage length of 10 inches was used to fulfill at least partly the A.S.T.M. standard specifications, namely with respect to annealed wires. The standard specifications for hard drawn wires requiring a gage length of 60 inches could not be met, because of lack of material and testing facilities. For the determination of tensile strength and elongation on the wires the American Society for Testing Materials standard methods were used.

The compression tests were made with a 600,000-pound Southwark-Emery tension machine with hydraulic drive. The load at which the first crack appeared on the outer shell surface of the cylinders was taken as first compressive strength, whereas the maximum

possible load which the specimens could take, was used for a second compressive strength. The changes in length and in diameter of the samples during the tests were observed by measuring the dimensions before and after testing.

An Olsen Izod impact testing machine was used for the impact tests. The impact strength could be obtained by a direct reading from the dial of the machine.

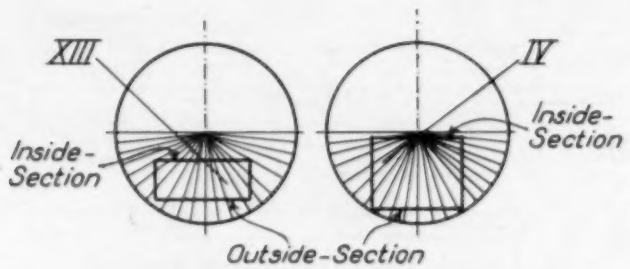


Fig. 4—Position of Test Cylinders in Raw Casting.

The electrical conductivity of the copper bars was checked by means of a Kelvin Double-Bridge, the conductivity of the wires was tested by means of a Wheatstone Bridge.

The density of the copper slugs was measured by pygnometer and checked against weight-volume measurements. The hardness was tested with an Alpha-3000-kilogram Brinell machine. A 10-mm. ball was used at a load of 500 kilograms, the load being applied for 30 seconds. The strain hardening compressions of the slugs were made with the aid of a hardened steel die and a hardened steel punch. A 50-ton Watson-Stillman press was used.

Fatigue tests were made on as-cast solid specimens in a high speed fatigue testing machine, type Wishart,[4] and on hard drawn wires in a wire fatigue testing machine, type Kenyon.[5] Both machines were operated according to the rotating beam principle at a speed of 9000 revolutions per minute.

Test Results

Tensile Tests—Table I gives the data of the tensile tests on the as-cast specimens, and Fig. 5 shows a ruptured specimen with its

[4]"Effect of Overload on the Fatigue Properties of Several Steels at Various Low Temperatures," by H. B. Wishart and S. W. Lyon, TRANSACTIONS, American Society for Metals, September 1937.

[5]"The Rotating Wire Arc Fatigue Machine for Testing of Small-Diameter Wire," by J. Kenyon, *Transactions*, American Society for Testing Materials, 1935, p. 156.

Table I
Tensile Data of As-Cast OFHC

No.	Casting	Yield Strength Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Per Cent Elongation in 2 Inches	Per Cent Reduction of Area
I A	A	14,000	23,200	43.6	55.0
I B	B	13,700	22,650	47.7	59.6
II A	A	14,400	23,300	44.4	57.0
II B	B	13,900	22,650	45.5	56.3

Table II
Tensile Data of Hard-Drawn and Annealed OFHC Wires, 0.060 Inch

Wires Produced by Direct Reduction Without Intermediate Anneals

		Gage Length of 2 Inches				Gage Length of 10 Inches			
		Tensile Strength Pounds Per Square Inch		Elongation Per Cent		Tensile Strength Pounds Per Square Inch		Elongation Per Cent	
No.	Casting	Hard	Annealed	Hard	Annealed	Hard	Annealed	Hard	Annealed
IX A	A	66,600	38,400	4.0	40.5	66,900	38,500	3.0	37.5
IX B	B	66,800	38,500	4.0	41.5	67,000	38,500	3.0	39.0
X A	A	66,900	38,300	4.0	42.5	67,000	38,600	3.5	40.5
X B	B	66,900	38,500	4.5	41.0	67,100	38,500	3.5	39.5
XI A	A	66,400	38,300	4.0	41.5	67,000	38,400	3.0	38.5
XI B	B	66,400	38,400	4.5	42.0	67,100	38,500	3.5	40.0
XII A	A	67,100	38,500	5.0	44.0	67,200	38,500	4.0	41.0
XII B	B	67,000	38,500	4.5	42.0	67,000	38,500	3.5	40.5

Wires Produced with Two Intermediate Anneals

		Gage Length of 2 Inches				Gage Length of 10 Inches			
		Tensile Strength Pounds Per Square Inch		Elongation Per Cent		Tensile Strength Pounds Per Square Inch		Elongation Per Cent	
No.	Casting	Hard	Annealed	Hard	Annealed	Hard	Annealed	Hard	Annealed
IX A	A	67,100	38,500	5.5	44.0	67,100	38,500	4.0	41.5
IX B	B	67,000	38,400	5.5	44.0	67,100	38,600	4.0	42.0
X A	A	66,900	38,400	5.0	43.0	67,000	38,600	4.0	41.5
X B	B	67,000	38,500	5.5	43.5	67,100	38,600	4.5	42.5
XI A	A	66,800	38,400	5.0	43.0	67,000	38,500	5.0	42.5
XI B	B	66,900	38,500	5.5	43.0	67,100	38,500	5.0	42.0
XII A	A	67,300	38,700	5.5	44.0	67,300	38,700	4.5	43.0
XII B	B	67,200	38,500	6.0	44.5	67,300	38,500	5.0	43.0

Table III
Compression Test Data of As-Cast OFHC

No.	Casting	Compressive Strength in Pounds Per Square Inch (First Crack)	Compressive Strength in Pounds Per Square Inch (Maximum Load)	Compression in Per Cent	Increase of Area in Per Cent
III A	A	222,000	319,000	64.8	189.1
III B	B	219,000	314,000	64.8	193.2
IV A	A	225,000	327,000	64.6	196.8
IV B	B	227,000	333,000	66.6	212.3

fracture. The tensile data of the hard drawn and annealed wires are summarized in Table II.

Compression Tests—Table III represents the data of the compression tests. Figs. 6 and 7 show the compression test cylinders before and after the test. Fig. 7 gives a picture of the typical shape

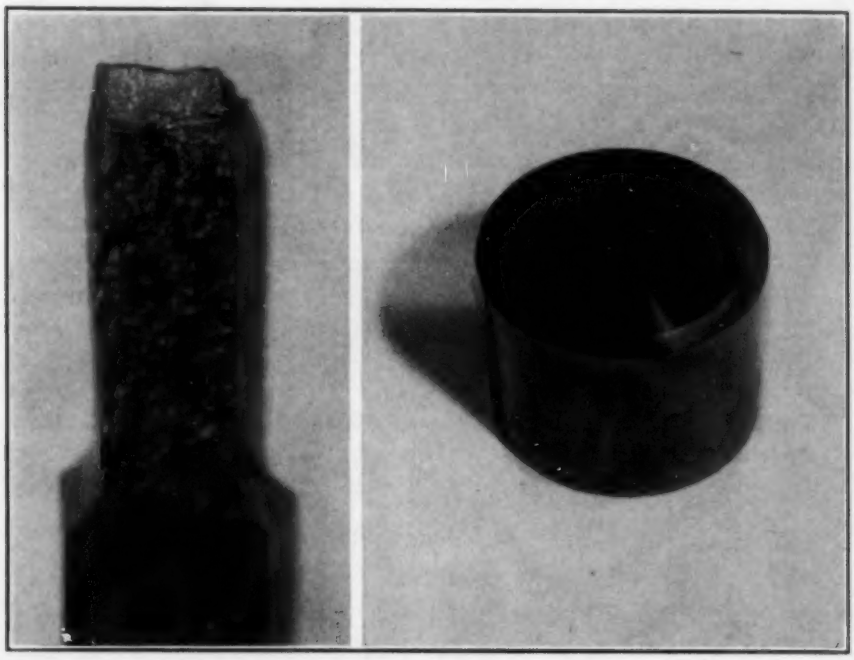


Fig. 5—(Left) Ruptured OFHC Tensile Specimen.
Fig. 6—(Right) Compression Test Specimen Before Testing.

of all tested specimens. This odd shape finds its explanation in the way the specimens were cut out of the casting, as explained in the sketch of Fig. 4. This sketch symbolizes the cut perpendicular to the columnar grains of the casting. Macrostructures of the two flat surfaces of the compressed specimen, as shown in Figs. 8 and 9, prove this fact.

Grain Structure—The macroscopic grain structure of the compressed cylinders are shown in Figs. 8 and 9. Investigations on the macroscopic grain structures of the Brinell test pieces in the as-cast and in the compressed condition are represented in Figs. 10, 11, 12 and 13.

The macrostructure of the two opposite flat surfaces and of a cut perpendicular to these planes of the Brinell slugs is shown in Figs. 10, 11 and 12. The sketch of Fig. 4 illustrates also for these specimens the location of the investigated samples in the casting and shows the difference in grain size. In the inside section the trans-

verse areas of grains are smaller than in the outside section. Fig. 13 represents a longitudinal section through a test slug after compression in a die. As the shape of the specimen was not deformed by compression, because of the lack of free movement in the die, the longitudinal sections of the grains appear the same as for the as-cast specimens.

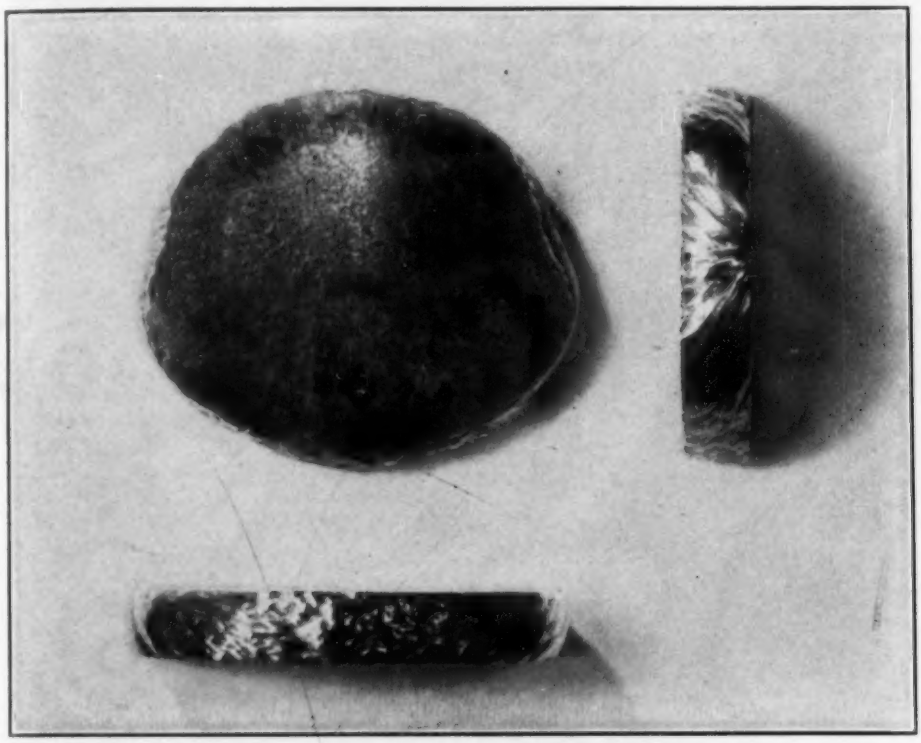


Fig. 7—Compression Test Specimen After Testing.

Fig. 14 shows the microstructure of an as-cast OFHC sample. No disharmony was found in comparison with the macrostructure. Very few pores, but no cuprous oxide inclusions could be detected. The macrostructures were developed with a 50 per cent dilute nitric acid and ammonium persulphate etching reagent, the microstructure with ammonia.

Density Tests—Density tests were made on as-cast slugs and on slugs which were strain hardened by a molding compression. Table IV shows the data of the tests on both types of material according to the above mentioned methods. No marked difference between the two types of material could be detected.

Hardness Tests—The results of the Brinell hardness tests are summarized in Table V and show a marked difference between the as-cast and the compressed material.

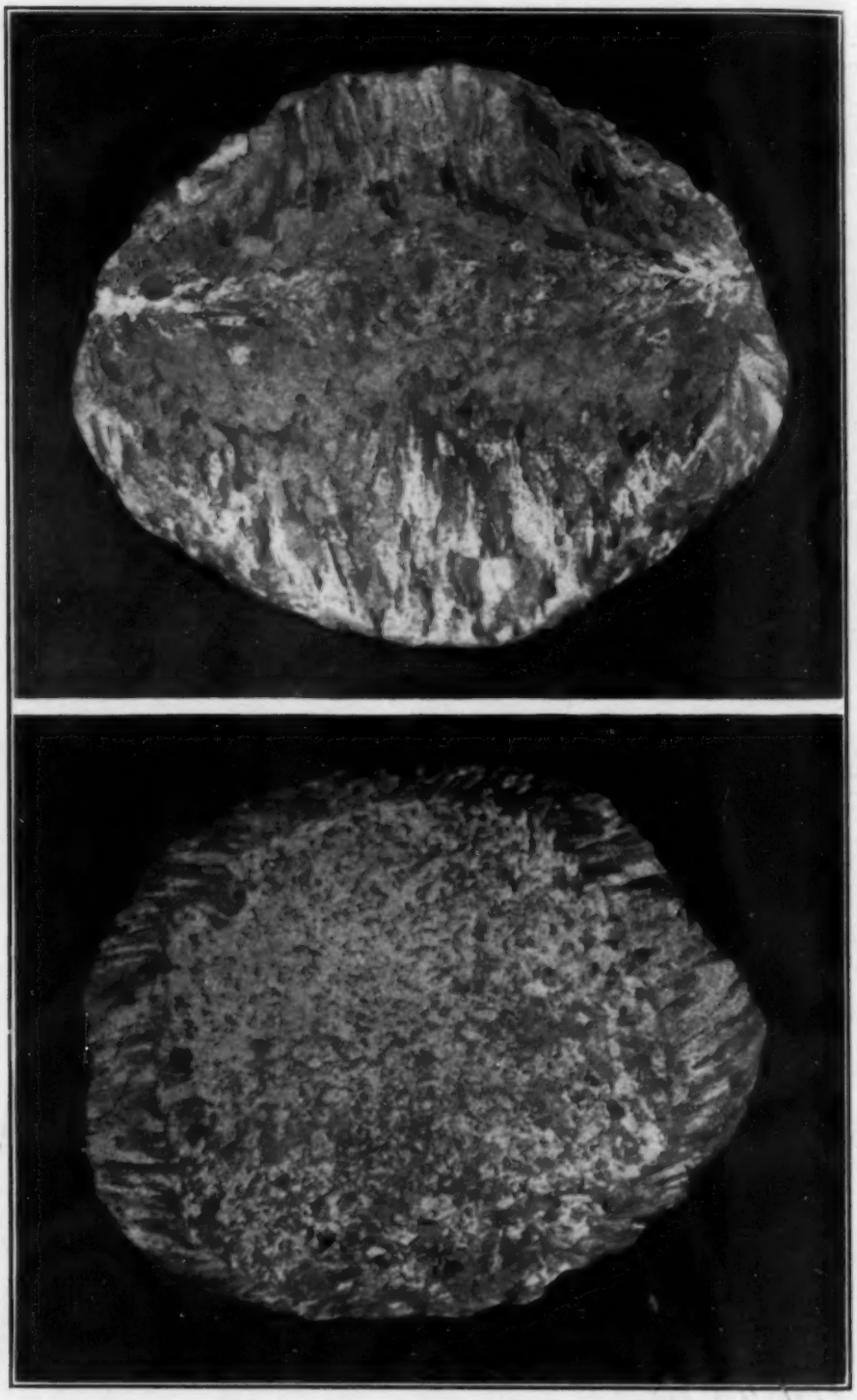


Fig. 8—Macrostructure of Compression Test Specimen After Testing. Inside Section.

Fig. 9—Macrostructure of Compression Test Specimen After Testing. Outside Section.

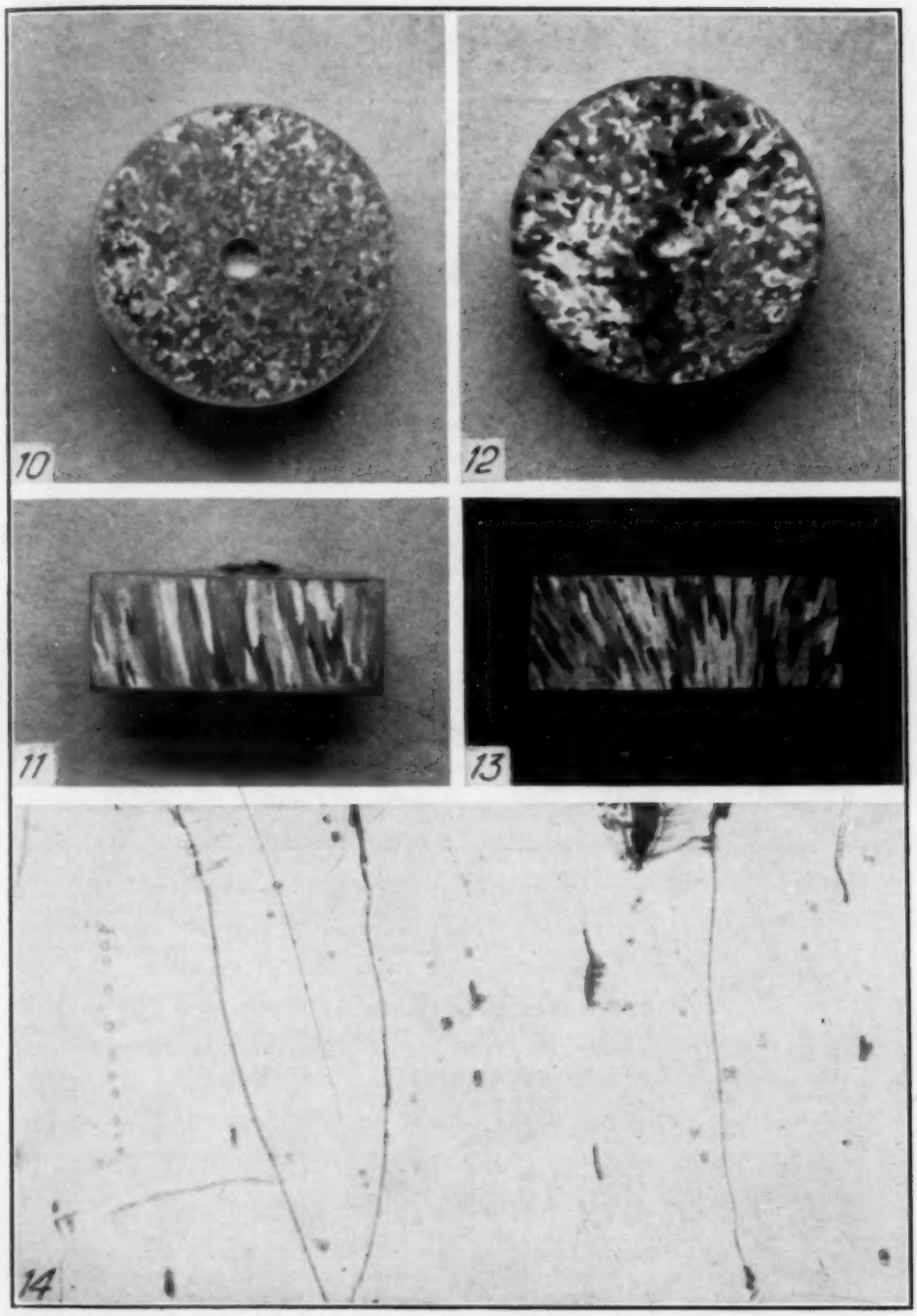


Fig. 10—Macrostructure of Hardness Test Specimen (as Cast). Inside Section.
Fig. 11—Macrostructure of Hardness Test Specimen: Longitudinal Section.
Fig. 12—Macrostructure of Hardness Test Specimen (as Cast). Outside Section.
Fig. 13—Macrostructure of Hardness Test Specimen After Compression in a Die. Longitudinal Section.
Fig. 14—Microstructure of Hardness Test Specimen (as Cast). Longitudinal Section. × 100.

Electrical Conductivity—Table VI gives the data of electrical conductivity tests on as-cast specimens and on hard and annealed

Table IV
Density Test Data of As-Cast and of Compressed OFHC

No.	Casting	Die Compression in Tons Per Square Inch	Density (Pygnometric Method) in Grams Per Cubic Centimeter	Density (Weight-Volume Method) in Grams Per Cubic Centimeter
XIII A	A	..	8.897	8.893
XIII B	B	..	8.904	8.909
XIV A	A	45	8.900	8.909
XIV B	B	45	8.910	8.914

Table V
Hardness Test Data of As-Cast and of Compressed OFHC

No.	Casting	Die-Compression in Tons Per Square Inch	Brinell-Hardness in Kilograms Per Square Millimeter
XIII A	A	..	38.0
XIII B	B	..	38.0
XIV A	A	45	50.0
XIV B	B	45	50.0

Table VI
Electrical Conductivity Test Data of As-Cast OFHC and of Hard-Drawn and Annealed OFHC Wires

		Electrical Conductivity of Cast OFHC		Electrical Conductivity of Wire 0.060 Inch Hard Drawn		Annealed	
No.	Casting	($\times 10^4$) in Centimeters Per Ohms and Square Centimeters	(vs. Standard) in Per Cent	($\times 10^4$) in Centimeters Per Ohms and Square Centimeters	(vs. Standard) in Per Cent	($\times 10^4$) in Centimeters Per Ohms and Square Centimeters	(vs. Standard) in Per Cent
IX A	A	57.0	98.3	57.4	99.0	58.9	101.7
IX B	B	57.2	98.6	57.5	99.2	58.9	101.7
X A	A	56.8	98.0	57.2	98.6	58.8	101.4
X B	B	57.0	98.3	57.5	99.2	58.8	101.4
XI A	A	56.9	98.2	57.3	98.0	58.9	101.7
XI B	B	57.2	98.6	57.5	99.2	59.0	101.8
XII A	A	57.2	98.6	57.6	99.4	59.0	101.8
XII B	B	57.3	98.8	57.7	99.6	59.1	102.0

wires. During the manufacture of the hard drawn wires two intermediate anneals took place, and the soft wires had two intermediate and one final annealing operation.

The conductivity testing results are uniform and do not show any dependence on the location of the original bars in the castings. All values are comparatively high if compared with previous investigations.[2]

Impact Tests—The data of the Izod impact tests are represented in Table VII. An impact bar after testing is shown in Fig. 15. A certain lack of uniformity of the test results can be seen, which is due to the way the specimens were cut out of the castings. The bars cut out of the outer shells had a higher impact strength than the bars of the inner zone, where the columnar grains

Table VII

Izod Impact Test Data of As-Cast OFHC

No.	Casting	Izod-Impact Strength (Vertical Direction) Foot-Pounds	Izod-Impact Strength (Horizontal Direction) Foot-Pounds	Izod-Impact Strength (Average) Foot-Pounds
V A	A	33.6	33.0	33.3
V B	B	28.5	26.6	27.6
VI A	A	24.5	24.7	24.6
VI B	B	23.7	26.3	25.0
VII A	A	29.2	29.0	29.1
VII B	B	28.8	31.6	30.2
VIII A	A	43.1	40.7	41.9
VIII B	B	34.0	32.2	33.1

were cut in smaller sections which provided more grain boundary areas. This result also is in accordance with results of impact tests on powder compacts, which were considerably lower with regard to the smaller grain size and the larger grain boundary areas of this material.

Fatigue Tests—The graphs of Fig. 16 show S-N curves of fatigue test results as obtained from as-cast specimens and from hard drawn wires. The diameter of the wires was 0.033 inch. The cast specimens were rotated in the open, while the wires were rotated in a damping medium consisting of mineral seal oil. As means of comparison the graphs also show the S-N curve of hard drawn OFHC copper as published by Rolle and Brace.[2] The lowering of the fatigue limit of the wire samples is probably due to different surface and fiber conditions of the wires if compared with the results of the solid specimens. The wire for the fatigue tests was produced by direct reduction, i.e., without any heat treatment and annealing.

Despite the difference in testing speed the author believes that the two S-N curves for the solid material are comparable. The two diagrams indicate a very distinct difference between the materials and this difference can by no means be laid entirely to difference in

testing speeds. The experience of other investigators, such as H. F. Moore and G. N. Krouse[6] have shown that high speed machines may give an endurance limit 10 per cent different from that given by lower speed machines. It may be assumed, therefore, that the difference in speed for the two types of copper tested would not produce any greater effect than to increase the endurance limit of the cast copper tested on the high speed machine by about 10 per cent above that value it would have had if tested at 3000 revolutions per minute.

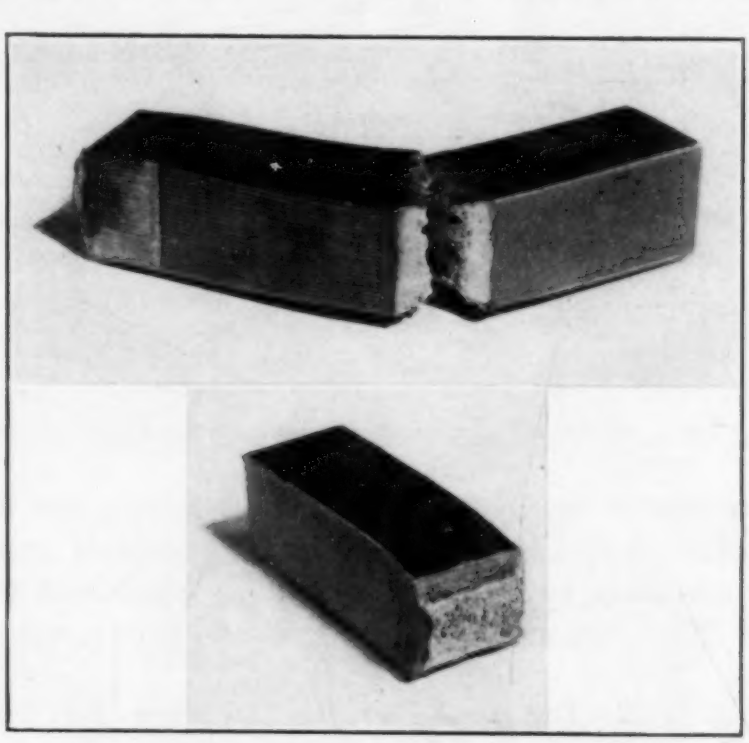


Fig. 15—Ruptured OFHC Izod Impact Test Specimen.

Critical Analysis of the Test Results

Tensile properties on as-cast OFHC and on hard drawn or annealed OFHC wires resulted in values which were well in accordance with previous investigations on the same matter, or with the American Society for Testing Materials standard specifications for copper wire.[7] The results were uniform and independent from the location of the specimens in the original casting.

The same is true for the compression tests. The rather unex-

[6] "Repeated-Stress (Fatigue) Testing Machines Used in the Materials Testing Laboratory of the University of Illinois," by H. F. Moore and G. N. Krouse, Circular No. 23 of the Engineering Experiment Station, University of Illinois, XXXI, March 1934.

[7] American Society for Testing Materials, Designations B1-27 and B3-27.

pected odd shapes of the samples after testing were caused by the particular way the specimens were machined out of the raw casting, and gave proof of the average values thus obtained. The influence of the die compression on the slugs was very slight with respect to their density as shown by the uniformity of the density tests.

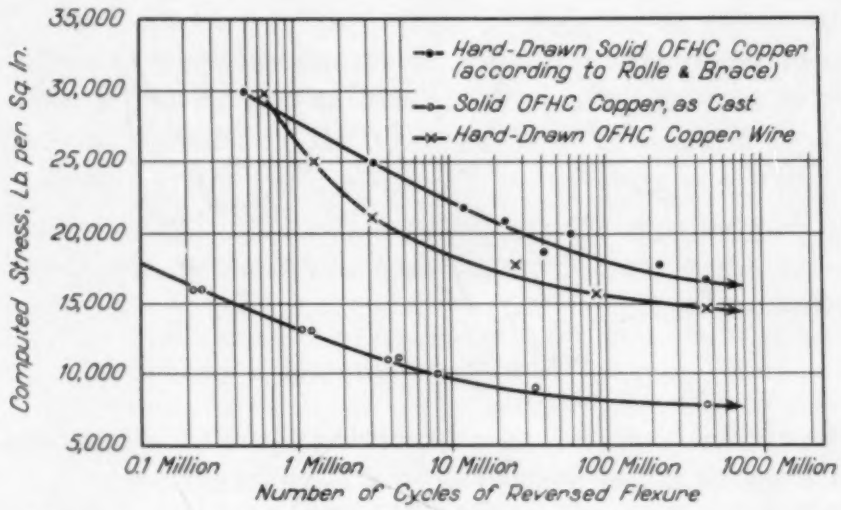


Fig. 16—Fatigue Test Values of as Cast OFHC and of Hard-drawn OFHC and OFHC Wire.

Brinell hardness tests, however, showed the influence of a molding compression and strain hardening more clearly. The hardness values of the compressed specimens did not, however, reach hardness values of real strain hardened copper, submitted to free movement during a rolling or drawing operation.

Macroscopic investigations of the grain structure could not reveal any difference between the compressed and the as-cast specimens, which also was not unexpected because of the typical kind of strain hardening the specimens were submitted to. Otherwise the grain structure gave its typical large crystalline grain structure in macroscopic and microscopic investigations.

Tests on electrical conductivity gave slightly higher results than the tests of previous investigations on OFHC copper.[2] They showed a considerable increase in conductivity after annealing of the wires.

Izod impact tests had somewhat inconsistent results and showed the influence of the location of the test bars in the original castings. The samples, in which the grains were cut in oblique sections, showed the highest impact strength.

Fatigue tests on as-cast specimens resulted in a S-N curve much

lower than the one known of hard drawn solid OFHC copper. This may be due chiefly to the fact that tensile strength too is considerably lower for as-cast than for hard drawn copper. On the other hand, the ratio between the tensile strength of the hard drawn solid specimens of the Rolle and Brace investigation and the tensile strength of the as-cast specimens of this investigation does not apply exactly to the ratio of the fatigue limits for the two types of material. The influence of the speed of rotation of the test pieces may count partly for this disharmony, but probably will be only of minor importance.

The S-N curve of hard drawn OFHC copper wire of 0.033 inch in diameter is slightly below the Rolle-Brace curve, which may be due to different surface conditions. Also the damping medium in which the wires were operated may contribute to the lowering of the endurance limit.

Acknowledgment

The above investigations were made as part of a dissertation for a Ph. D. degree in the Department of Metallurgy, School of Mines, Columbia University, New York.

The author is indebted to the United States Metals Refining Co., for furnishing the raw material. He also is indebted to the Department of Metallurgy and to the Testing Laboratories in the Department of Civil Engineering of Columbia University for the use of equipment, and to the Hardy Metallurgical Co. for the permission to publish the results.

DISCUSSION

Written Discussion: By H. B. Wishart, metallurgist, Carnegie-Illinois Steel Corp., Gary, Ind.

Mr. Goetzel in his paper has presented information that is of interest in a comparison of the physical properties of OFHC copper in the as-cast and drawn state.

In Fig. 16 a comparison is made between the S-N diagrams obtained from as-cast and hard drawn solid copper. The diagram of the as-cast copper was obtained from specimens tested in a high speed fatigue machine while the diagram of the hard drawn copper was obtained from specimens tested in a slow speed fatigue machine. The writer, from previous experience, agrees with the author that little error is induced by the difference in speed of testing. There is, however, the possibility that greater error is caused by the comparison of metal of different casts.

The S-N diagrams show that the trend of the endurance limit is to increase with drawing of the copper. It is of interest to note the endurance ratios, ratio of endurance limit to tensile strength, of the copper in the three states. The ratios of the as-cast copper and the hard drawn solid copper were about 0.3 while the ratio of the hard drawn copper wire was in the neighborhood of 0.2. Such a difference in ratios shows that the endurance limit of the copper wire was much lower than the copper in its other two states when compared to the tensile strength. It would be of interest to know if the variation in ratios was caused in any way by the difference in drawing or in the surface condition of the specimens tested.

Written Discussion: By John N. Kenyon, instructor in civil engineering, Columbia University, New York.

Fatigue data cannot be properly evaluated without due consideration being given to the methods of test and to the mechanical treatments of the materials. It should also be kept clearly in mind that fatigue failures occur within the "elastic range" of the material and not in the "plastic range" which is above the elastic limit.

The Rolle-Brace curve, Fig. 16, was obtained with the Farmer machine and with a well polished fatigue specimen about 0.30 inch in diameter. Fatigue fracture was confined to the center of the specimen. Mr. Goetzel used the arc machine and an 0.037 inch diameter wire with the usual surface irregularities due to the drawing operation. The wire test specimen was subjected to nearly equal fatigue stress over a length of about 12 inches and fracture naturally occurred at some weaker point within this length. These considerations, together with the fact that the two materials had somewhat dissimilar mechanical treatments justify a statement that the two curves check with reasonable accuracy.

Oral Discussion

L. W. KEMPF:[8] I am sure we are indebted to Mr. Goetzel for initiating comparisons between castings and material from compressed powders and I am also sure that many will join with me in hoping that this comparison might be carried even somewhat farther to the investigation of some characteristics which have not been touched upon very extensively in the present paper; e.g., it would be interesting to know whether hard drawn or hard rolled copper shows the same recrystallizing characteristics when produced from a casting as when produced from compressed slugs.

I must confess that there is a sentence in Mr. Kenyon's discussion which is not entirely clear to me, perhaps because I have not given it enough thought. The sentence I refer to is the one which says: "It also should be kept clearly in mind that fatigue failures occur within the elastic range of the material and not in the plastic range which is above the elastic limit." Of course I suppose we should go back and start with the definition of what the fatigue limit of such a material as copper is, but I will not try to do that. I think that all of us have encountered apparent endurance limits well above the elastic

[8]Research metallurgist, Aluminum Company of America, Cleveland.

limit of the specific material being examined. I am more familiar with aluminum than any other materials and, on the basis of 500 million cycles, we frequently encounter endurance limits well above the original elastic limit of the material. Of course it can be said that the fatigue limit was above the elastic limit of the material as it ended the test because under such circumstances the material hardens during testing. At least that is my interpretation, but nevertheless Mr. Kenyon's statement is somewhat ambiguous as it stands.

SIDNEY ROLLE:[9] I think from the experience we have had in making fatigue tests, such as have been referred to in Mr. Goetzel's paper, that the previous history of the material used for the test specimen has a marked bearing on the results obtained. The S-N curve, according to Rolle and Brace, shows the result of fatigue test made in the conventional manner on hard drawn OFHC copper rod previously hot-rolled from wire bars. (The tensile strength of the copper tested was 56,750 pounds per square inch.) Rod made in this manner very likely has a more homogeneous structure than that obtainable by cold working cast material. As I understand it, Mr. Goetzel cold-rolled sections cut from the material we furnished him and then drew the cold-rolled rod into wire without preliminary or intermediate annealing. I am of the opinion that such procedure works the metal quite differently from when it is fabricated in the usual manner and, therefore, has a decided bearing on the results.

I agree with Mr. Goetzel that high speed fatigue tests are quite good and the results fall within about 10 per cent of those obtained by standard methods. On the other hand, results on individual test pieces and even results on groups or batches vary a great deal more than 10 per cent, so I should like to see the results of more extensive tests using a large number of specimens. I think these results will show that while the method of making the fatigue test, that is whether high speed or low speed, may be disregarded, the method of fabricating the material should be taken into consideration.

JOHN N. KENYON:[10] I would like to discuss briefly the endurance properties of copper in the light of service performance as a possible lead for further tests on these materials. A certain municipal railway is using OFHC copper for rail bonds and believes that in so doing service breaks have been eliminated. It is believed that the oxygen-free copper has higher endurance properties where there are vibrational effects and a corrosive environment. I cannot vouch for the accuracy of the supposition, having made no tests, but I do believe that it suggests work along the line of corrosion-fatigue.

At Columbia we test small diameter steel wire by the arc method wherein the wire, bent to arc curvature, is rotated and vibrational effects dampened out in an oil bath. I have recently made tests on a group of small diameter steel wires having various metallic coatings. When tested in oil, the fatigue curves of both the coated and the uncoated wires are very closely grouped. By substituting for the oil a mildly corrosive medium like distilled water, I got a wide variation and the wire that had no protective coating showed by far the lowest endurance limit. In other words, under noncorrosive conditions the

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[9]Assistant manager, The Scomet Engineering Co., New York, N. Y.

[10]Instructor in civil engineering, Columbia University, New York.

curves were closely grouped, but when there was a slight corrosive element present, they were widely scattered.

Now if copper wire materials were tested by the arc method in an oil bath, we would no doubt obtain a closely grouped set of curves. Probably the oxygen-free copper would give a higher curve since any metal free of oxide should have better endurance properties. If the tests were made in some controlled aqueous solution, to simulate corrosive conditions, we might obtain a widely scattered set of curves. I believe that such a test would more nearly give the true service qualities of these materials. I hope to make such a test within the next year.

Author's Reply

Mr. Wishart's question, whether the difference in the ratios of tensile strength and fatigue strength of the solid copper specimens, either as cast or hard drawn, versus the hard drawn wire is due to the different manufacture of the test specimens or due to different surface conditions, is quite interesting. It is very likely that both factors play an important part. On the one hand, as Mr. Rolle already pointed out, the manufacture of the wires was done by cold rolling and drawing directly without any annealing, whereas in the case of the Rolle-Brace investigation the specimens were reduced from much larger ingots, the common way, first by hot rolling and then by drawing with several intermediate annealings. Therefore, this difference might well account for the variation in the ratios of the different materials. I also agree with Mr. Rolle that it would be quite worthwhile and conclusive to repeat fatigue investigations on larger style commercial material thus giving the base for better average data. On the other hand, however, the wire samples were generally more sensitive against slight surface imperfections, particularly due to the severe cold reduction of the tested material. These minute surface imperfections easily might have caused a certain inferiority of the fatigue limit of the tested copper wire.

Mr. Kenyon is quite correct in pointing out that in the case of the wire fatigue tests the specimens were subjected to a fatigue stress over a length of approximately 12 inches which, of course, provides a better chance that the fatigue failure starts at the weakest point of the sample. In the case of the solid specimens, however, the fatigue fractures were strictly confined to the center of the specimens, regardless of the degree of perfection of the remaining parts of the specimens. It also might be of interest to point out that the ratio of tensile strength and fatigue strength of the hard drawn Rolle-Brace specimens was only 0.30 against a ratio of 0.34 for the as-cast specimens of this investigation. This checks closely with the statement that the higher testing speed results in up to 10 per cent higher fatigue limits if compared with tests done with an ordinary slow operating machine. Disregarding this point it can be stated that the S-N curve for the cast specimens is by no means too low, but rather slightly too high or almost correct. Mr. Kenyon's statement about the corrosion resistance of high-grade copper, such as our oxygen-free material, and about the beneficial influence of an oil bath as protecting medium is very interesting and eliminates the assumption that the

damping medium used in this research might have lowered the results to a certain degree.

I agree with Mr. Kempf that it certainly would be very interesting to check recrystallizing characteristics of molded and compressed cast slugs and compare these results with the well known recrystallization phenomena of hard drawn or hard rolled copper. It is likely that there will be a marked difference between the two types of hard worked materials with regard to their different performance under the work hardening pressure, i.e., with regard to their ability to move freely in the one case, but to be restricted from free movement in the other case. In reference to Mr. Kempf's statement about the occurrence of fatigue failures above the elastic limit I incline to endorse him to a certain point, as otherwise it would not be clear to me why we reach rather high endurance characteristics with copper, in spite of the fact that the elastic limit of this material is remarkably low.

IDENTIFICATION OF INCLUSIONS IN STEEL BY THE USE OF REFLECTED POLARIZED LIGHT

By M. A. Scheil, Mary Baeyertz, and J. R. Vilella

Abstract

This paper discusses the use of reflected polarized light in metallography. The method of examining metallographic specimens for inclusion identification is discussed and a table of properties lists the distinctions to be observed in the more common inclusion minerals.

The investigator is reminded of certain limitations in this method of identification and it is the object of this article to emphasize some of these in order that the full use of reflected polarized light may be realized in the correct interpretation of the results.

The advantages of using reflected polarized light to distinguish inclusions are pointed out, such as distinction of opaque, translucent, and fully transparent inclusions; observations of isotropic or anisotropic behavior, and transmitted light color of translucent inclusions.

The identification of certain opaque inclusions is made more conclusive by a table of supplementary etching tests.

The paper concludes with an up-to-date bibliography of the subject.

Introduction

THE use of reflected polarized light is a comparatively new tool in metallography. Transmitted polarized light has been in use for some time to determine strain in transparent substances (photoelasticity). The determination of the constituents in mineralogical thin sections by the use of polarized light is well known in technological practice, and the science of mineralogy has thus far described 261 minerals as opaque, of which 93 are shown by the microscope to be either mixtures of minerals or doubtful species (1)[1]. The use of a polarizing microscope is no longer confined to the field

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

Of the authors, M. A. Scheil is research metallurgist, department of metallurgical research, A. O. Smith Corp., Milwaukee; M. Baeyertz is assistant research engineer, Carnegie-Illinois Steel Corp., South Works, Chicago; and Joseph R. Vilella is associated with research laboratories, United States Steel Corp., Kearny, N. J. Manuscript received October 3, 1938.

of petrography due to the pioneer work of Dr. Emile Chamot. It is now used to advantage in the field of chemical microscopy (2), and slag investigations have been carried out and the mineral composition determined with its aid (27, 28). Research workers in various branches of science have given testimony to the possibilities of investigation with this tool. Although the use of polarized light was recommended for the study of opaque substances as early as 1909 by Konigsberger (3), it has not been used in metallography until quite recently. A few treatises have appeared from time to time dealing with reflected polarized light in the study of opaque ores and metals (4, 5, 6, 7, 8, 9, 10, 11, 12, 32, 33, 34).

The use of reflected polarized light to identify opaque substances has not been as outstanding as the effects obtained with transparent materials. Until quite recently all of the polarizing microscopes for reflected light did not furnish truly linear but slightly elliptical polarized light in the plane of the object. The amount of this elliptical polarization was small but in some cases was sufficient to produce abnormal extinction effects. Furthermore, the perfection of polarization was disturbed by reason of numerous parasitical reflections and refractions, due to the lenses and vertical illuminator, which modified slightly the polarized cone reaching the analyser. Thus birefringent substances were not always totally extinguished and isotropic substances were not always absolutely black between crossed nicols (22), particularly if the latter were transparent or translucent. In recent years the vertical illuminator has been much improved in the homogenization of the field for observations between crossed nicols, and improvements in this direction are being continued (36 to 49 inclusive).

During the past six to seven years efforts have been made by various investigators to apply polarized light to metallography, as a further means of identifying inclusions, structural components and phases. In the development of what is practically a new branch of science, it is not surprising that the results obtained by earlier investigators were not always in agreement. The investigations that have been reported (13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23) show the utility of polarized light in the study of nonmetallic inclusions.

During the evolution of this new tool, for metallographic investigation, research workers have realized that certain limitations must be placed upon its use in order to arrive at the correct interpretation of the results given. In order that the investigator shall not

obtain an erroneous identification of the inclusions to be studied, he should have in mind these limitations before attempting to make full use of reflected polarized light. He should also realize that this method, of itself, is often not conclusive and, therefore, should be used with the aid of other methods of identification such as etching. The nature of the optical phenomena observed is dependent, to a significant extent, on the design of the optical system.

In technological studies on steel, identification of inclusions is being actively studied, in the hope of accumulating more knowledge of the reactions that occur in a known practice.

The original contribution in this field was the etching scheme by Campbell, Comstock and Wohrman for identifying various oxides, sulphides, silicates and other constituents by systematic etching tests and microscopic examination.

This method is time consuming and in many instances difficulties are encountered with etching tests (18, 24), particularly for small and complex inclusions, so that it is desirable to accomplish as much as possible on the "as polished" surface. For this purpose illumination by reflected polarized light with crossed nicols is finding much use. Examination of the polished inclusions in reflected polarized light minimizes surface reflections of transparent and translucent substances and permits the light which penetrates them to be observed where it emerges after internal reflections.

The color of these reflections is the same as would be obtained on viewing the same inclusions by transmitted light, except in the case of substances of strong birefringence. In the latter instance the color of the reflected light may sometimes be modified by polarization colors. The determination of the color of translucent inclusions is a valuable aid in identification. Information on the isotropy or anisotropy of the substances investigated may sometimes, although not always, be obtained.

By this means a rapid and useful method has been developed for technical practice which distinguishes opaque, translucent, and fully transparent inclusions and which by means of color effects and birefringence is capable of supplying additional evidence.

Polishing the Inclusions for Microscopic Examination

The preparation of the sample for the study of inclusions is of great importance to the success of the examination. There are several good methods of preparing the surface, and any method of

polishing which gives the following results should be entirely satisfactory:

1. A smooth and level metal surface,
2. retention of inclusions, and
3. a satisfactory polish on the surface of the inclusions, free from scratches, distorted surface layers and films.

The surface films produced in polishing inclusions have not generally been established as influencing to a great extent the polarization effects. However, the influence of surface films will become more important as methods and observations become more refined. The matter of surface films in polishing sulphide inclusions has been observed to be especially important. The sample for examination of inclusions may be mounted in bakelite or hard resin to facilitate hand polishing or automatic polishing of small specimens. The usual preliminary polishing steps are employed, such as coarse grinding and fine grinding on the metallographic dry papers No. 1, 0, 00 and 000. Frequently, used 000 paper rubbed over with paraffin or graphite is employed. The use of graphite is cautioned against, at least for inexperienced polishers, as this practice frequently leads to embedded graphite in the surface layers of metal during polishing. Such embedded graphite, after final polishing with alumina or magnesia, may have the appearance of an inclusion and will appear anisotropic with crossed nicols.

The final polishing is carried out on broadcloth laps using levigated alumina or magnesia. After final polishing it is important to properly clean and dry the prepared surface. Dried water spots produce bright areas under crossed nicols, and clumps of the polishing media or dirt tend to sparkle on the otherwise opaque polished surface, and may lead to erroneous conclusions. It is not advisable to etch the prepared polished surface before microscopic examination, with polarized light, because the surface roughness produced by etching causes scattering reflections which are confusing and may lead to grating polarization. Heat tinted specimens should not be used since such treatment may cause oxide films on the surface of the inclusions.

Method of Examination

After proper preparation of the polished surface the section is first thoroughly examined under ordinary reflected white light to determine the size, shape, color by ordinary reflected light, and dis-

tribution of the inclusions. The section is then examined with reflected plane polarized light with nicols crossed. Two determinations are made, namely, the determination of the color by transmitted light and the examination for evidence of anisotropic behavior.

Path of the Rays in Microscopes for Use with Reflected Plane Polarized Light

The examination of inclusions with reflected plane polarized light may be made with the usual types of metallurgical microscopes, if accessory equipment with which to obtain and analyze the plane polarized light is added, and certain precautions are observed. Some manufacturers now make such equipment in holders especially designed to fit into the optical train of microscopes of their own manufacture.

The usual source of light for a metallurgical microscope is an arc or filament lamp. Light from either of these sources may be considered as vibrating in all directions normal to the light beam. In order to obtain plane polarized light (vibrating in one direction only), it is necessary to interpose a polarizer in the light beam. The polarizer should be situated between the light source and the field stop or aperture stop. The polarizer should always be protected by a heat absorbing glass placed between it and the light, in the case of an arc lamp. With small incandescent lamps this is not necessary.

The polarizer, commonly termed "nicol prism", (the actual prisms used are of the so-called Glan-Thompson type) is so constructed that when a beam of unpolarized light is passed into it, the resulting transmitted beam is plane polarized. The vibration direction of the light emerging from the polarizer can be regulated by rotating the polarizer around the axis of the optical train. The polarizer should be rotated until its vibration direction is either perpendicular or parallel to the axis of tilting of the reflector in the vertical illuminator, and then be kept in that position during microscopic observations. If the polarizer deviates only a fraction of a degree from this position, elliptical polarization will be introduced.

From the vertical illuminator, usually a prism of special design, the plane polarized light is projected through the objective to the specimen surface from which it is reflected into the microscope to the eyepiece which forms the visible image. Before being viewed at the eyepiece, the light reflected from the specimen is passed

through an analyser. The analyser may be placed between the vertical illuminator and the eyepiece or a cap nicol, placed over the eyepiece, may be used instead.

The analyser functions in a similar manner as the polarizer. Thus only plane polarized light which vibrates in the direction of the analyser can pass through it. When the vibration direction of the analyser is set at 90 degrees to the vibration direction of the polarizer, the nicols are said to be "crossed". With crossed nicols the plane polarized light which passes the polarizer, if reflected unchanged to the analyser, cannot pass the analyser and the field of view is dark. If the character of the polarization is altered, i.e., if the plane polarized light becomes elliptically polarized, or the vibration direction of the polarized light is changed, then light will pass the analyser.

Change in the character of polarization and resolution into components of the vibration direction of plane polarized light can be caused by reflecting surfaces in the optical train, so it is advisable to eliminate them or place them so that the minimum effect is obtained. Rotation of the specimen should be obtained by rotating the stage on which the specimen is fixed. For this purpose the microscope should be equipped with a rotatable stage, preferably graduated in degrees. Cross haired eyepieces, representing planes of vibration of the nicols, are very desirable.

Brightness, Color and Surface Anomalies

Brightness or transmitted light color may usually be observed in a few inclusions if a number are present and if the inclusions are transparent or reasonably translucent.

The transmitted light is observed because incident plane polarized light is refracted into and transmitted through the translucent inclusions and is reflected from the inclusion-metal interface, from a crack in the inclusion upon which back reflections can take place, or, in inclusions which contain more than one phase, from the phase boundaries within the inclusion. The light coming out from the inclusion is no longer plane polarized as it was before entering the inclusion. Random reflections from the inclusion-metal interface and other internal interfaces cause the character of original plane polarized light to be changed so that light passes the analyser. This darkfield effect has no connection with anisotropism (both isotropic and anisotropic substances show it) and particular care should be

taken not to confuse it with anisotropic behavior. If the nicols are parallel, appearance of the inclusions is similar to that observed by ordinary reflected light. The general illumination from the incident beam as reflected from the polished metal surface is so great that the much weaker transmitted light from the inclusion cannot be observed or is seen only indistinctly. This small amount of light from the internal reflection through the inclusion may be seen by crossing the analyser nicol, which efficiently removes the surface reflected light and if the inclusion is sufficiently translucent its transmitted color can be identified provided that the birefringence of the inclusion mineral is not high. Under certain conditions of internal reflection in minerals of high birefringence, the colors observed with crossed nicols are interference colors rather than the transmitted light color of the mineral. If the substance is translucent the transmitted light color may be complicated, with certain anisotropic inclusions, by reason of high absorption for certain wave lengths which vary in certain crystallographic directions of crystalline inclusions (reflection pleochroism).

Aside from these confusing effects in certain anisotropic inclusions, the determination of the transmitted light color depends on the following factors:

1. The dimensions of the inclusion,
2. the orientation of the reflecting surface with respect to the vibration planes of the nicols,
3. the translucence of the inclusion,
4. the method of polishing (freedom from polish-film, scratches, and differences in level of different constituents),
5. the crystallographic orientation of any anisotropic crystals in the inclusion from which internal reflection takes place, and
6. the numerical aperture and type of objective.

Thus reflection through a relatively thin layer of a highly translucent substance from a metal-inclusion interface or, in inclusions which contain more than one phase, from a highly reflecting phase-translucent phase interface will give the maximum reflected light for observation, provided that the reflecting surface is properly placed with respect to the vibration directions of the nicols. The difficulties of determination of the transmitted light color increase markedly as the translucence of the inclusions decreases. An objective of high numerical aperture sometimes alters the apparent brightness and color of the inclusion regardless of whether it is translucent or

opaque. This is probably due to the fact that less of the plane polarized light can be reflected unchanged, because of the possibility of introducing elliptical polarization caused by objectives used for high magnification. The light gathering properties of the high numerical aperture lenses make any particular inclusion, only slightly translucent, appear brighter than with lower numerical aperture lenses. With opaque inclusions, especially, immersion objectives modify the apparent reflectivity. The apparent reflectivity increases as the difference between the refractive index of the inclusion and the refractive index of the surrounding material increases. Portevin and Castro (18) have observed that examination under a dry objective generally gives more violet-shaded colors than an immersion objective does. At times the dimensions of the inclusion and the surface polish offer disturbing effects to a proper identification. In certain very hard inclusions of small dimensions, their surface is not always polished plane and is frequently convex. When examined by reflected polarized light, diffraction and depolarization phenomena are set up at the edge of the inclusion. Likewise, pits and scratches on isotropic surfaces improperly prepared can produce effects which may be mistaken for anisotropic behavior.

Heat tinting, etching or other surface coloring to produce contrast by affecting the metallic surface is not recommended for examination in reflected polarized light as these methods can produce oxide filming on the surface of the inclusion, causing polarization phenomena. This can alter the original plane of vibration of the incident plane polarized light to produce psuedo-anisotropic effects. A. M. Gaudin (25) has used a method of selective iridescent filming to identify opaque minerals in ordinary reflected light.

Anisotropic Behavior

Examination of the inclusions by reflected polarized light between crossed nicols may enable the investigator to distinguish the isotropic vitreous (no crystal system) and crystalline substances (cubic system) from the anisotropic substances (all other crystalline systems). A cubic crystal is the same in all dimensions, having equal axes while other systems have either unequal dimensions of axes or inclined axes so they are not the same when looked at in different orientations.

Substances showing one index of refraction are called isotropic

and regardless of their orientation they appear to have no effect upon the light which enters them, other than single refraction and the absorption giving rise to their transmitted light color. Examples of isotropic substances are those which crystallize in the cubic system (including most metals), and those which can be classified as amorphous, (glasses).

Anisotropic substances exhibit more than one index of refraction, i.e., anisotropic materials possess the property of resolving the vibrations of light which enters them into component vibrations which are plane polarized but vibrate in different planes and travel at different rates through the crystal. The directions of the reflected planes of light which correspond to the planes of vibration in an anisotropic substance are sometimes called "axes of elasticity" or "vibration axes". The difference between the indices of the rays gives the strength of birefringence and is characterized as strong or weak. The identification of anisotropy in inclusions of weak birefringence, that are transparent or translucent, is especially difficult owing to the disturbing effects of internal reflection. Thus, materials of weak birefringence appear to behave the same as isotropic ones under reflected polarized light with crossed nicols. Opaque isotropic inclusions will remain dark in all positions when the specimen is rotated in the plane of its polished surface, the reason for this being that the plane polarized light suffers no change in its state of polarization when reflected vertically from any plane surface of the isotropic substance. Thus the direction of vibration is unchanged and if the nicols are crossed the reflected light will be extinguished by the analyser.

Anisotropic substances, when examined with completely linearly polarized reflected light, disturb the condition of the plane polarized light beam reflected vertically by their surface. These disturbances may show themselves in two ways. Most important of these changes is the resolution into components of the plane of vibration. Due to this resolution into components the reflected light will have a component in the vibration direction of the analyser and some light will pass through it. Rotation of properly oriented crystals of the anisotropic substance will cause the reflected light to vary from extinction to maximum brightness four times in 360 degrees rotation of the stage, in contrast to opaque isotropic substances which remain dark between crossed nicols during a 360-degree rotation. Only in the positions in which the principal directions of vibration (axes of

optical elasticity) of the anisotropic surface coincide with the vibration directions of the nicols will there be extinction. At these positions there is no resolution into components of the plane of vibration of the reflected light.

The incoming linear polarized light can also be reflected as circular or elliptical polarized light, two special cases of the resolution into components, which is produced because of the birefringence of the material. These are the principal disturbances which cause a change in the nature of the polarized light if brightness of the beam has been restored. These two effects can be distinguished from each other by means of compensators which can be added between the polarizer and analyser. The function of the compensator is to introduce any desired phase difference into polarized light. A quartz wedge is an example. Thus by means of compensators, polarized light with any amount of ellipticity may be changed to plane polarized light which is the only type of polarized light capable of being entirely absorbed by the analyser nicol.

These disturbances of the plane of vibration can vary in regard to the degree to which they can be evidenced so that we observe a strong or a weak birefringence.

The magnitude of these effects in most cases is rather small, particularly with inclusions exhibiting weak birefringence, so that it is of great importance that the incoming polarized light be wholly plane polarized, as otherwise any small elliptical polarization effect from the inclusion may be missed, and the absence of observable anisotropic behavior under crossed nicols will not indicate that the inclusion may be actually isotropic. Translucent anisotropic materials will show four extinctions, however, if not so fine-grained as to show continuous brightness. This abnormality in behavior has been observed in steels containing crystalline inclusions of alumina. These are hard and brittle and are difficult to polish. Often the individual grains are dislodged during polishing and produce the comet-tailed scratches. When these inclusions are examined under crossed nicols they are bright but show no difference in brightness when the sample is rotated on the stage. This anomalous behavior is thought to be due to scattered reflection of light (darkfield effect) at the places where minute particles had been torn out from the inclusions (20). By reason of this scattered light producing a general illumination of the particles, the inclusions do not extinguish when rotated, as they should from their hexagonal structure. For similar

reasons these inclusions, when well polished and of crystalline form, may remain bright during rotation of the stage with crossed nicols, because the crystals are small, highly translucent, and are usually backed by a metal-inclusion interface which is very irregular in contour so that in any position of the stage there is some part of the interface in such a position that it will reflect light which can pass the analyser.

In all aluminum deoxidized steels there are a variety of inclusions which may be formed ranging from globules, which may be fluxed with FeO and silicates, to hard Al_2O_3 particles which show rough crystal outline. Contamination of alumina with FeO apparently does not cause the alumina to become opaque unless the melt is oxidized. In melts high in FeO, to which a small amount of aluminum has been added, there is a range in which the inclusions formed are black globules (*26*), small but larger than the ordinary alumina particles, and which show evidence of having been liquid at some time after their formation. These are ferrous aluminate inclusions in various stages of fluxing with the ferrous oxide and are of opaque isotropic nature (19).

It has been shown that a translucent birefringent substance can produce anisotropic behavior in two ways. One of these is the behavior of the substance toward the plane polarized light which is transmitted through the inclusion and reflected from the metal-inclusion interface, a crack in the inclusion or, in inclusions which contain more than one phase, from a phase boundary. Any true anisotropic behavior thus observed by transmission is superimposed on the depolarization by reflection from these interfaces. Unless the birefringence is fairly strong these effects are usually not noticed. The effects of birefringence can be effectively separated from depolarization by reflection from the reflecting interfaces only when the inclusions are of reasonable size and translucence, have a fairly strong birefringence and have well developed crystal faces which are both properly oriented with respect to the optic axis or axes of the crystal and lie in a plane perpendicular to the reflected plane polarized beam.

It has also been shown that an inclusion can exhibit a body color due to light transmitted by it and a polarization color due to anisotropic effects in surface reflection. Furthermore, if both are present, the one that has the greatest intensity will predominate. Therefore, if an inclusion is observed to have a certain color, rotation of the stage will differentiate between body color and polarization colors or

pleochroic reflection, but not between surface polarization, interior birefringence, and pleochroic reflection. If the color is transmitted, (the true color of the translucent inclusion), rotation will not affect it. If the color is due to anisotropic behavior, either surface or interior, the brightness will vary with the orientation upon rotation of the stage. The color may be of the primary Newton Series or the secondary or some higher order depending on the birefringence and thickness of the material producing the vibration.

Dayton (16) shows that small or large particles of cuprous oxide in copper will appear to have a light blue color (their true "surface color") under ordinary reflected light. By reflected plane polarized light small particles of cuprous oxide show a ruby red color, which is the body color of this oxide in transmitted light. This effect has been observed by several investigators, notably von Schwarz (35) who has published photomicrographs in natural colors. On examining a thick section of cuprous oxide, only parts that were in fragments showed the transmitted red color. All the thicker sections were dark under reflected polarized light because of absorption of any light which entered them. The cracks in the oxide formed surfaces for back reflections which enabled the transmitted light color to be obtained. Further, it was determined, by rotation of the stage, that the color in polarized light changed with the position of the stage and the crystals therefore were anisotropic. Cuprous oxide inclusions in copper were thus shown to exhibit an anisotropic effect which is obscured by the much greater intensity of the transmitted color of the translucent inclusions.

Dayton believes that the anisotropic behavior of cuprous oxide inclusions is due to the formation of a surface layer of cupric oxide, caused by oxidation in the atmosphere, which is anisotropic. For this reason, indications of surface anisotropy do not always qualify the inclusion as an anisotropic substance. The possibility of a surface film should be realized as a certain limitation which must be placed upon the correct interpretation of the result. Others have ascribed similar effects to surface phenomena, notably Beilby (30) who worked with sodium nitrate crystals on polished cleavage planes.

Another anisotropic effect, commented on by Portevin and Castro (18), should be mentioned. They refer to glassy or transparent vitreous globular isotropic inclusions which have been elongated by hot working. These inclusions when polished tend to show a pseudo-anisotropic appearance in polarized light. The elongated

inclusions light up and are extinguished four times for each revolution of the microscopic stage, the positions of extinction being those where the axis of elongation of the inclusion coincides with the planes of vibration of the nicols, and the positions of illumination being at 45 degrees from these axes. The direct interpretation of this anomalous behavior, between crossed nicols, of a transparent vitreous inclusion elongated by rolling may lead the observer to think that the inclusion is anisotropic. The existence of anisotropic character should not be based on observations of thin elongated inclusions.

Isotropic Behavior

Opaque isotropy has already been discussed under anisotropic behavior. Examples of opaque inclusions showing isotropic behavior are ferrous oxide inclusions in rimming steels and in Armco iron. These inclusions are rarely pure FeO and are usually mixtures, as FeO-MnO, and contain sulphides. Manganous sulphide inclusions usually contain some FeS and are generally opaque. Manganous oxide inclusions are rarely pure and contain ferrous oxide. These are usually opaque but with increasing MnO the transparency becomes more pronounced and the color changes. Such inclusions may show distinct green to brown color.

Translucent to opaque inclusions exhibiting isotropic behavior may be bright or colored at one or more positions during rotation of the stage. Many isotropic inclusions may also show alternate brightness and darkness as the result of the orientation of the reflecting interfaces with respect to the vibration planes of the nicols. This effect has been mistakenly ascribed to strain by some authors and referred to as a strain-anisotropic condition.

Chromite ($FeO \cdot Cr_2O_3$) is an example of an inclusion which may possess slight transparency when very thin. The material is isotropic and the transmitted color is red with polarized light. Thicker inclusions may be entirely opaque.

Fully transparent and translucent globular glassy inclusions in metals are generally isotropic and in polarized light exhibit the dark cross phenomena. Such inclusions are usually rich in silica and are isotropic. However, of the crystalline inclusion phases which contain silica, some are isotropic and some anisotropic.

The dark optical cross, frequently observed in spherical glassy silicate inclusions in cast or weld metal, when observed with reflected

plane polarized light crossed nicols, is not a distinctive property of silica glass. The black cross remains stationary with respect to the cross hairs in the microscope when the stage is rotated and the brightness of the inclusion does not alter during 360 degrees rotation. This is due to reflection polarization at the inner metal surface. The contour and character of the reflecting interface between the inclusion and the metal must be smooth. Any roughness of the reflecting surfaces causes a destruction of the effect because of random reflections introduced by this roughness. The only part which the glassy inclusion plays is to be isotropic and of such translucence that it does not interfere with these reflections. Gas pockets, voids or holes of similar shape, if the air-metal interface is untarnished and smooth, give similar effects. Therefore, the observer should be sure an inclusion is present before making the assumption that a globular, clear, transparent silica glass exists.

Of more significance, however, is the transmitted light color from these glassy inclusions. For instance pure silica inclusions rarely occur in deoxidized steels and in nearly all cases are mixtures of silicates such as manganous and ferrous silicates. The globules vary in color according to the degree of deoxidation of the steel. Those consisting of pure or nearly pure silica are clear and colorless. However, very small quantities of iron oxide are sufficient to give them a red color, while larger quantities make them opaque. Larsen (26) has stated that it is doubtful that TiO_2 or CrO inclusions ever occur free from considerable amounts of FeO or SiO_2.

In examining glassy inclusions in weld metal Hoyt and Scheil (17) have observed transmitted colors in globular cast silicates that exhibited the optical cross and have associated this coloration by reflected plane polarized light with crossed nicols to contamination with certain metallic oxides that are miscible in the silicates. "Milky" appearance in glassy inclusions can be caused by the presence of two or more phases in finely divided state, because of precipitation within the glass on cooling. One of the phases must be translucent but, aside from this one condition, the physical state of aggregation of the phases and their relative amounts in the inclusion are much more influential in causing this effect than the character of the phases themselves.

The transmitted colors of these glassy inclusions show wide ranges of variation in both color and translucence depending on their composition. For instance, chromium silicates, which are trans-

parent, may show a green to orange color, the green silicates being richer in chromium and the orange or brown silicates richer in iron. Korber and Oelsen (29) have reported that certain vitreous chromium slags were dark blue in color, the color being caused by small amounts of CrO. Manganous and ferrous silicates may be colored a reddish brown to a dark green or greenish brown. Calcium silicate inclusions when free from other contaminating oxides are "milky". Thus it becomes evident that the transmitted color of the glassy silicate inclusions may indicate to the observer the presence of other contaminating oxides which may be useful as a means of determining steel quality by a rapid examination of the inclusions. Conclusions drawn from observations of this kind should always have the knowledge that has already been obtained through complete chemical analysis. This should include a quantitative description of the oxide inclusions which will then make it possible for the observer to distinguish the contaminated silicates.

Identification Tests for Inclusions

The following scheme of identification contains tables of properties of substances which may be encountered as nonmetallic inclusions in the examination of steels and irons. It should be noted that inclusions in metals rarely consist of a single pure component and their properties are therefore unlikely to coincide precisely with those of the minerals to which they are related. Further, the methods just described for the examination of polished metallographic specimens are sometimes incapable of distinguishing some of their optical properties. For more detailed information on the minerals given in the tables, and for information on other possible "inclusion minerals", the investigator is referred to (50, 51, 52).

The minerals described, however, will help to identify inclusions on the basis of optical character. Certain inclusions derived from refractories occur as minerals and the use of these tables will help to identify such inclusions which might be identified as other substances if the scheme for etching identification tests were used alone.

The tables also include the characteristics, which may be observed by reflected plane polarized light with crossed nicols, of inclusions in steels and irons similar to the composition of the minerals.

The properties of the minerals described in the tables (a) to (f) inclusive are for minerals of the particular allotropic modification as

stated and do not correspond in all cases to the properties of inclusions that may occur in steels and irons of quite similar chemical composition.

For the convenience of the investigator an etching scheme is also included to enable the identification of certain opaque oxides frequently encountered as well as other isotropic substances which can sometimes be identified by their color and shape and can be further distinguished by their etching characteristics.

The investigator should make all of his observations by reflected plane polarized light with crossed nicols, first, before applying the etching tests to his sample for identification purposes.

Proper use of the scheme should employ the following procedure:

1. Examination of the inclusions "as polished" with ordinary reflected white light at X 200, X 500 or X 1000; to observe the size, shape, reflected light color, and distribution of the inclusions.

2. Selection of several representative fields for further investigations by reflected plane polarized light with crossed nicols for observation of isotropic or anisotropic behavior, opaqueness or translucency, and transmitted light color.

3. Complete identification of opaque inclusions and others when in doubt with appropriate etching tests.

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Distinctions To Be Observed For The Identification Of Inclusions In Steels And Irons With Reflected Polarized Light

(1) Name and Formula
  (a) Crystal system
  (b) Melting point
  (c) Hardness (Mohs' Scale)
  (d) Color by reflected white light

(e) Color by transmitted white light (plane polarized light crossed nicols).
(f) Index of refraction
(g) Common occurrence
(h) Remarks

Inclusion Minerals Which Always Remain Dark During 360 Degrees Rotation

(1) Ferrous Oxide, wüstite, FeO
(a) Isometric
(b) 1360 degrees Cent. (2480 degrees Fahr.)
(c) 5.5-6.5
(d) Medium grey
(e) Opaque
(g) In scale, and as more or less rounded single phase globules, in rimming and similar steels low in silicon and manganese.
(h) Somewhat malleable at S R T (steel rolling temperatures).

(2) Magnetite, $FeO \cdot Fe_2O_3$
(a) Isometric
(b) 1327-80 degrees Cent. (2421-2516 degrees Fahr.)
(c) 5.5-6.5
(d) Light grey
(e) Opaque
(g) In scale
(h) Not malleable at S R T

(3) Titanium Nitride, TiN
(a) Isometric
(c) 9-10
(d) Yellow
(e) Opaque
(g) In steels and irons treated with ferrotitanium.
(h) Not malleable at S R T. May contain TiC in solid solution. Color in reflected white light varies from yellow to pink to violet with increasing carbon content. Pink sometimes called cyano-nitride. The inclusions are strongly angular and easily pitted in polishing.

(4) Zirconium Nitride, ZrN
(a) Isometric
(b) 2950 degrees Cent. (5342 degrees Fahr.)

(d) Yellow
(e) Opaque
(g) In steels and irons treated with ferrozirconium.
(h) Not malleable at S R T. May contain ZrC in solid solution which produces varying colors by reflected white light: Orange, brown, violet, blue. The inclusions are strongly angular and they may be distinguished from TiN by etching tests. They are softer and easier to polish than TiN.

(5) Vanadium Nitride, VN
(a) Isometric
(b) 2000 degrees Cent. (3632 degrees Fahr.)
(c) 9-10
(d) Pink
(e) Opaque
(g) In vanadium steels. Inclusions resemble titanium cyanonitride.

Translucent Isotropic Inclusion Minerals

(1) Manganous Oxide, Manganosite, MnO
(a) Isometric
(b) 1700 degrees Cent. (3092 degrees Fahr.)
(c) 5-6
(d) Very dark grey
(e) Green
(f) N = 2.16 (Li)
(g) In steels and irons high in manganese which have not been deoxidized with other more effective deoxidizers, e.g. aluminum and silicon.
(h) Somewhat malleable at S R T. Usually contains more or less FeO in solid solution. Color by reflected white light changes from dark grey to medium grey with increase in FeO. Color by transmitted light changes from green to red or brownish red to opaque with increase in FeO.

(2) Manganous Sulphide, Alabandite, MnS
(a) Isometric
(b) 1620 degrees Cent. (2948 degrees Fahr.)
(c) 3.5-4
(d) Medium grey
(e) Green
(f) N = 2.70 (Li)

(g) Steels and irons except those with very low manganese content.

(h) Very slightly malleable at S R T, malleability increases with increase in FeO in solid solution. Usually contains FeS in solid solution. In stainless steels probably also contains Cr in solid solution. Color by reflected white light changes from medium grey to greyish white, with pearly luster, with increase in FeS. Color by transmitted white light changes from green to greenish yellow or brown to opaque with increase in FeS.

(3) Iron Aluminate, Hercynite, $FeO \cdot Al_2O_3$

(a) Isometric

(b) Above 1700 degrees Cent. (3092 degrees Fahr.)

(c) 7.5-8

(d) Medium to dark grey

(e) Colorless, green, yellow brown, reddish brown, opaque when rich in iron oxides.

(f) N = 1.80

(g) In steels and irons treated with aluminum and in some inclusions derived from refractories.

(h) Not malleable at S R T. Change in color and translucence due to solid solution. Opaque varieties are lighter grey by reflected white light. Frequently occurs as equiaxed euhedral crystals. Not as difficult to polish as inclusions rich in Al_2O_3.

(4) Chromite, $FeO \cdot Cr_2O_3$

(a) Isometric

(b) Above 1780 degrees Cent. (3235 degrees Fahr.).

(c) 5.5

(d) Medium grey

(e) Red, reddish brown, yellowish brown, or opaque depending on the thickness.

(f) N = 2.07-2.16

(g) In steels and irons which contain chromium.

(h) Not malleable at S R T. Frequently occurs as equiaxed euhedral crystals, and also observed to be of eutectic nature. These inclusions are easily polished.

(5) Silica Glasses

(a) Non-crystalline

(b) Variable

(c) Approximately 7
(d) Light to very dark grey, sometimes with bright internal reflections.
(e) Colorless or all colors depending on contamination with other oxides.
(f) Variable
(g) In steels and irons which contain silicon which have not been thoroughly deoxidized with other more effective deoxidizers, e.g. aluminum; and in some inclusions derived from refractories.
(h) Varying degrees of malleability at S R T. May be more or less milky because of precipitation of other minerals in finely divided state within the glass on cooling. In cast or weld metals transparent spherical glassy silicates exhibit the dark optical cross by transmitted white light.

Opaque Minerals Showing Anisotropic Behavior

(1) Ferrous Sulphide, Troilite, FeS
(a) Hexagonal
(b) 1180-1190 degrees Cent. (2156-74 degrees Fahr.)
(c) 3-4
(d) Light tan or yellow
(e) Opaque
(g) In steels and irons very low in manganese
(h) Malleable at S R T. Under reflected plane polarized light with nicols crossed, properly oriented grains show four extinctions in 360 degrees.

Translucent Anisotropic Minerals with Weak Birefringence

(1) Alumina, Corundum, Al_2O_3
(a) Hexagonal
(b) 2050 degrees Cent. (3722 degrees Fahr.)
(c) 9
(d) Medium grey
(e) Colorless
(f) No = 1.77, Ne = 1.76 (Na)
(g) In steels and irons treated with aluminum, and in some inclusions derived from refractories.
(h) Not malleable at S R T. Color by transmitted light

changed variously by impurities in solid solution. Occurs as equiaxed or elongated grains with irregular surfaces, or euhedral crystals. These have a tendency to group together in clumps or small clouds of particles. During rolling or forging these groups are formed into irregular rows of particles in the direction of working. These inclusions are rarely pure and may contain FeO and SiO_2. The inclusions rich in Al_2O_3 are difficult to polish and frequently their anisotropic behavior is masked by reason of their transparency and highly reflecting metal-inclusion interface, or by rounding the edge of the cavities left by their removal.

(2) Mullite, $3Al_2O_3 \cdot 2SiO_2$
- (a) Orthorhombic
- (b) 1816 degrees Cent. (3301 degrees Fahr.)
- (c) 7.5
- (d) Medium to dark grey
- (e) Colorless, pink
- (f) Ng = 1.654, Nm = 1.644, Np = 1.642
- (h) Frequently occurs as long euhedral crystals in glass inclusions.

(3) Quartz, SiO_2
- (a) Hexagonal
- (b) 1600-1750 degrees Cent. (2912-3182 degrees Fahr.)
- (c) 7
- (d) Medium to dark grey
- (e) Colorless
- (f) Ne = 1.55, No = 1.54

(4) Cristobalite, SiO_2
- (a) Pseudo-isometric (tetragonal?)
- (b) 1696 degrees Cent. (3085 degrees Fahr.)
- (c) 6-7
- (d) Medium to dark grey
- (e) Colorless
- (f) No = 1.487, Ne = 1.484
- (h) Usually associated with glass.

Translucent Anisotropic Minerals with Strong Birefringence

(1) Fayalite, $2FeO \cdot SiO_2$
- (a) Orthorhombic

(b) 1205 degrees Cent. (2201 degrees Fahr.)
(c) 6.5
(d) Medium to dark grey
(e) Colorless, light green, yellowish green, yellowish brown.
(f) Ng = 1.886, Nm = 1.887, Np = 1.835
(h) Frequently contains $2MnO \cdot SiO_2$ in solid solution.

(2) Ferric Oxide, Hematite, Fe_2O_3
(a) Hexagonal
(c) 5
(d) Medium to light grey
(f) No = 3.22, Ne = 2.94 (Na)
(g) Frequently occurs as outer layer of scale.

(3) Chromic Oxide, Cr_2O_3
(a) Hexagonal
(b) 1900 degrees Cent. (3452 degrees Fahr.)
(d) Medium to light grey
(e) Green, depending on the thickness
(f) N = 2.5 ±
(g) In stainless steels and other high chromium materials
(h) Not malleable at S R T. These inclusions are harder than chromite.

(4) Aluminum Nitride, ALN
(a) Hexagonal
(b) 2150-2200 degrees Cent. (3902-92 degrees Fahr.)
(d) Dark to very dark grey
(f) Birefringence high (indices not available). Often show brilliant polarization colors.
(g) In chromium produced by the aluminothermic process and in chromium steels containing aluminum.
(h) Frequently occurs as euhedral crystals.

Scheme For Etching Identification Tests

Appearance with Reflected White Light—× 200, × 500, × 1000

Grey or Black Inclusions

Etch 10 sec. in 10% Alcoholic Nitric Acid

More Contrast
(a) FeO in FeO·FeS eutectic darkened

Unattacked
Etch 5 min. in 10% chromic acid in H_2O

Attacked
(a) Removes FeS·MnS rich in MnS
(b) Darkens FeO·MnO

Unattacked
Etch 5 min. in boiling alkaline sodium picrate

Attacked
(a) Removes FeS·MnS rich in MnS
(b) Removes FeO·MnO

Unattacked
Etch 5 min. in 5% Alcoholic HCl

Attacked
(a) Removes FeO·FeS
(b) Removes FeO
(c) Removes balance FeO·MnO
(d) Removes $MnO \cdot SiO_2$

Unattacked
Etch 10 min. in a 20% aqueous solution of HF

Attacked
(a) Removes $FeO \cdot SiO_2$
(b) Removes $CaO \cdot SiO_2$
(c) Removes Some Siliceous alumina

Unattacked
(a) Al_2O_3, $FeO \cdot Al_2O_3$ and (FeO, MnO) Al_2O_3
(b) Chromite ($FeO \cdot Cr_2O_3$) Etch 5 min. in boiling 10% H_2SO_4 and 1% $KMnO_4$ and lightly repolish

Attacked
(a) Chromite ($FeO \cdot Cr_2O_3$) Isotropic: red to brown by transmitted light

Unattacked
(a) Chromic oxide (Cr_2O_3) Anisotropic: purplish grey by re-reflected light, bright green by transmitted light.
(b) Ferrous aluminate ($FeO \cdot Al_2O_3$) opaque isotropic: light grey

Yellow, Tan or Pink Inclusions

Etch 10 min. in boiling Alkaline Sodium Picrate Solution

Attacked
(a) Removes FeS (pale yellow)

Unattacked
Etch 10 min. 20% aqueous HF

Attacked
(a) Removes zirconium nitride (yellow cubes)
(b) Removes zirconium sulphide (tan crystals)

Unattacked
(a) Titanium nitride (yellow cubes)
(b) Titanium cyano nitride (violet: strongly angular, easily pitted in polishing)
(c) Titanium carbo nitride (blue cubes)

..... In stainless steel and ferro-chromium—not applicable to ordinary alloys of lower Cr Content.

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EFFECTS OF SPECIAL ALLOY ADDITIONS TO STAINLESS STEELS

By Russell Franks

Abstract

This paper gives a general discussion of the effects of the most important additions to stainless steels. It points out that while stainless steels have served quite satisfactorily, the desire to widen their field of application has required modification by addition of special alloying elements. The paper discusses the best procedure for machining the steels. It describes the beneficial effects of nitrogen on the plain chromium steels; the use of titanium and columbium in inhibiting intergranular corrosion in the chromium-nickel steels; and the effects of molybdenum in retarding the development of pitting and contact corrosion. Data are shown on the effect of manganese in improving the hot working characteristics of the modified chromium-nickel steels. It is finally pointed out that such additions are not made to complicate the constitution of these steels, but are made to render them more serviceable to the industry.

IN the early development of stainless steels the aim was to obtain a metal free of the staining and progressive rusting that occurs when ordinary steel is exposed to the atmosphere. Brearley secured this result in a hardened, tempered, and polished 13 per cent chromium and 0.30 per cent carbon steel; Haynes in steels of higher chromium and lower carbon contents; and Strauss in low carbon higher chromium steels that contained nickel. Each investigator determined that the steels would resist oxidizing acids, and in addition Strauss was impressed with the high ductility and toughness of the chromium-nickel steels. While some evidence was presented on the utility of these steels in the chemical industry, these early workers were chiefly concerned with permanence of surface under atmospheric conditions. The steels were referred to as "rust-proof materials."

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Today, however, stainless steels are considered from a much broader viewpoint. With the development of special equipment and processes in industry to produce chemicals that a few years ago could be considered only from a laboratory standpoint, new requirements have been put upon the steels. To be sure the inherent properties of the heat treated steels have in general met the requirements, but it is not always possible to retain the annealed state throughout fabrication, and often it is impractical to anneal the fabricated product. The difficulties arising from the inability to retain the annealed state or its equivalent may cause a loss in physical properties, or corrosion resistance, or both. In other instances the difficulties may be due to an inherent lack of physical requirements or corrosion resistance demanded of the steel by the user. It is such conditions that have forced the metallurgist to modify the steels and not his desire to make them more complex from the standpoint of constitution. This paper discusses the reasons for making a few of the important additions to the chromium and chromium-nickel steels, and their effects.

Plain Chromium Steels

Possibly the earliest modification of the plain chromium steels concerned an improvement in machinability. Shortly after the low carbon 12 to 15 per cent chromium steels of the rustless iron type were made available for commercial consumption, it was found that they could not be turned, sawed, drilled, tapped, etc., according to the practice employed on ordinary carbon and low alloy steels. The annealed chromium steels, because of high toughness, had a marked tendency to gall, tear, and develop excessive friction during cutting, even though they were relatively soft. This condition has been partially relieved by the use of cooling liquids, decreasing the cutting speeds, and providing the tools with about 5 per cent more top rake to permit the chip to clear the surface of the tool during cutting. Further improvement can be obtained by increasing the Brinell hardness number of the annealed steels from 150 to about 200 by cold drawing or heat treating to decrease toughness. The metal in this condition can be cut with high speed steel tools ground with an increased top rake at a speed equivalent to about 60 per cent of that for ordinary steel. Cutting angles on taps, drills, dies, and the like cannot be changed so readily, and in operations involving these tools the speed should be reduced to about 40 per cent of that for ordinary steel to obtain satisfactory cutting.

Perhaps the best solution to the machining problem is found by modifying the compositions of the steels. Additions of 0.25 to 0.30 per cent sulphur to the low carbon 12 to 15 per cent chromium steels are effective. While corrosion resistance is decreased, sulphur addition reduces toughness and practically eliminates the high frictional effect encountered in machining, and the steel can be cut at approximately the same speeds used for ordinary steels. Improvement in machinability is obtained by adding 0.60 per cent molybdenum or 0.15 per cent selenium, and corrosion resistance is not greatly changed. Molybdenum sulphide is added to improve machinability. In this instance the steel contains a maximum of 0.65 per cent molybdenum and 0.40 per cent sulphur.

In machining any of the high chromium steels except those modified by addition agents, the cutting speeds must be reduced. Sometimes the desired production can be maintained with the normal steels by increasing the feed, but if this is impractical decreased production must be accepted as a necessity, and the best results are obtainable with high speed steel cutting tools.

The low carbon 12 to 14 per cent chromium steels are also modified by the addition of aluminum and tungsten. Aluminum is added to reduce air hardening and is usually present to the extent of about 0.25 per cent, while the tungsten is added to improve strength at high temperatures. Tungsten is normally present to the extent of about 3 per cent. It has been claimed that the tungsten-bearing steels are especially suited for oil refinery service.

Steels containing 12 to 14 per cent chromium and 0.30 to 0.40 per cent carbon have been widely applied for cutlery purposes. However, investigation has shown that better edge-holding properties can be obtained in a steel containing 16 to 18 per cent chromium with 0.60 to 0.80 per cent carbon. The corrosion resistance and cutting properties of these steels are further improved by adding about 0.75 per cent molybdenum. While molybdenum has introduced no serious handicap, the resulting steels require treatment at a slightly higher hardening temperature of about 1000 degrees Cent. (1830 degrees Fahr.) rather than the usual temperature of 950 degrees Cent. (1740 degrees Fahr.) in order to secure the necessary hardness. The steels containing molybdenum should not be held too long at the higher hardening temperature as grain growth will occur and detrimentally affect cutting quality.

The highly useful heat resisting 25 per cent chromium steels

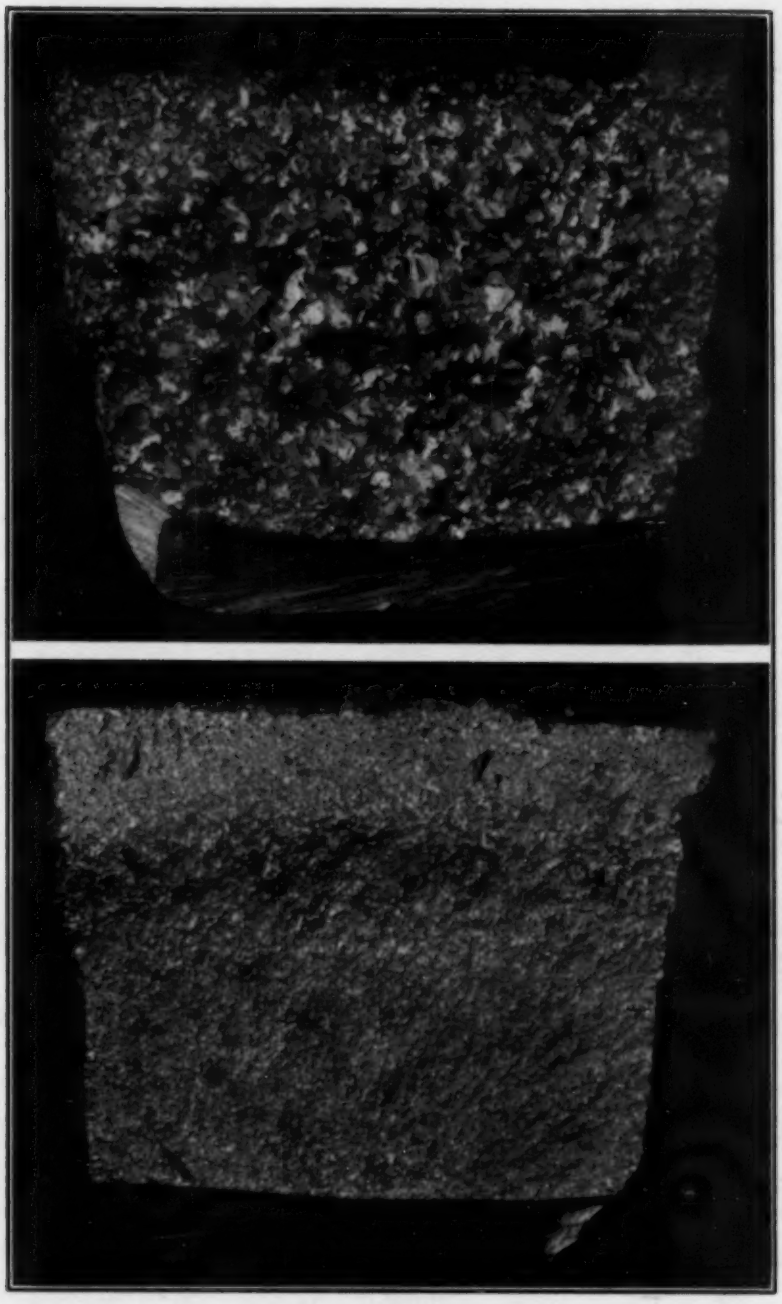


Fig. 1—The Casting at the Top Contains 25 Per Cent Chromium, 0.19 Per Cent Carbon and 0.035 Per Cent Nitrogen, While the Casting at the Bottom Has Similar Chromium and Carbon Contents but Contains 0.20 Per Cent Nitrogen. (Natural Size.)

have been modified to impart better hot working properties and to eliminate brittleness after annealing. The difficulties encountered on forging or rolling these steels are undoubtedly connected in part with the large grains existing in the cast metal, while the brittleness at normal temperatures after annealing is due to the simultaneous

occurrence of both small and large grains in the wrought product. As shown in Fig. 1 nitrogen, when added in the form of high nitrogen ferrochromium, reduces the grain size of the cast steels. The reduction in grain size permits the steels to be rolled on blooming

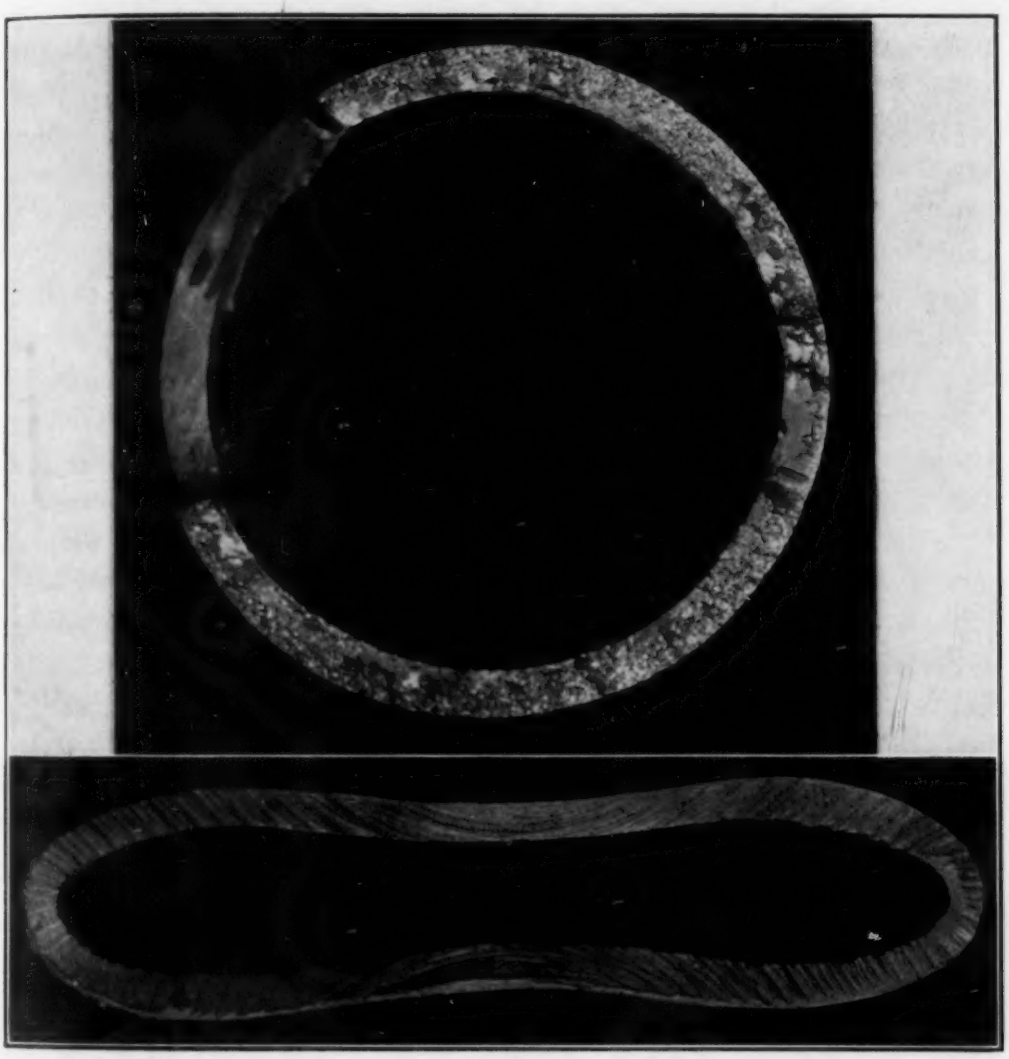


Fig. 2—The 3-Inch Diameter Fractured Tube at the Top Was Made from a 25 Per Cent Chromium Steel Containing 0.15 Per Cent Carbon and 0.04 Per Cent Nitrogen. The Flattened Tube at the Bottom Was Made from a Steel of Similar Chromium and Carbon Contents Containing 0.17 Per Cent Nitrogen. (Natural Size.)

mills without danger of excessive cracking, which has markedly increased the recovery of finished products from ingots; and indeed the use of nitrogen has made possible the handling of large ingots of the steels. Thus the addition of 0.15 to 0.20 per cent nitrogen has practically eliminated the variation of grain size in wrought annealed 25 per cent chromium steels. See Fig. 2.

In Fig. 2, the photograph at the top clearly shows that the low nitrogen 25 per cent chromium steel seamless tube, which was in the annealed condition, varied appreciably in grain size. This tube fractured as shown, in an attempt to straighten it after annealing by quenching from 900 degrees Cent. (1650 degrees Fahr.). The photograph at the bottom of the high nitrogen steel tube shows that this metal was quite ductile after annealing in the same manner, which is attributed to the uniformly fine grain of the annealed steel. This improvement was accomplished without sacrifice of either corrosion or heat resistance.

Chromium-Nickel Steels

The low carbon wrought austenitic chromium-nickel steels of the 18-8 type have received considerable attention and are unquestionably among the most useful materials for resisting heat and corrosion. The steels possess a high degree of corrosion resistance and are exceedingly ductile and tough in the annealed state. However, when heat is applied during fabrication or in service, their extraordinary properties may be affected even though the corroding medium is of a mild nature. The difficulty is not due to lack of resistance to general corrosion but to localized corrosion in which only certain areas are affected. The types of corrosion referred to are intergranular and pit corrosion. In order to obtain the best service under the most severe conditions of heat and corrosion it has been found desirable to make certain modifications in composition.

The first of these types is brought about by the decomposition of the austenitic constituent. Decomposition may take place if the metal is heated to temperatures between 300 and 800 degrees Cent. (570 and 1470 degrees Fahr.). The effect is not instantaneous but is accumulative. The period of time required varies with the different temperatures. At temperatures in the range 595 to 870 degrees Cent. (1100 to 1400 degrees Fahr.) periods of 3 to 10 minutes are sufficient, while at temperatures between 300 and 595 degrees Cent. (570 and 1100 degrees Fahr.) longer heating periods are required. Decomposition may take place in such engineering processes as welding of relatively thick sections or heating for purposes of fabrication. Since decomposition greatly lowers the corrosion resistance in grain boundary regions, exposure to relatively mild corroding media may cause metal that is otherwise perfectly satisfactory to fail. It is thus imperative that the susceptibility of

the chromium-nickel steels to this type of attack be recognized when their application is concerned.

A positive method for overcoming this difficulty is to modify the composition of the steels. Their carbon content is important, but a mere lowering of the carbon content to 0.07 per cent or somewhat less does not solve the problem. The most effective method consists of adding columbium, although titanium is effectively used under certain conditions.

When titanium is used it must be present to the extent of at least six times the carbon content, and the steel must be given a stabilizing heat treatment within the range 850-900 degrees Cent. (1560-1650 degrees Fahr.) for a period of from 2 to 4 hours, followed by air cooling. While the steels treated in this manner are relatively free of intergranular attack their resistance to general corrosion is not so satisfactory as that of the fully annealed plain 18-8 steels, and when wet corrosion is involved they must be used with caution. On the other hand, if corrosion at high temperature is involved satisfactory resistance may be expected. The titanium-bearing steels are unsuitable for use as welding rods. The titanium is oxidized, and the resulting weld will not be immune to intergranular attack. This means that to secure satisfactory operation, the titanium-bearing steels must be welded with rods containing columbium.

As previously stated, columbium offers an effective solution to the problem of intergranular corrosion. When complete immunity to intergranular attack is required between 300 and 800 degrees Cent. (1570 and 1470 degrees Fahr.), the columbium content should be equivalent to at least ten times the carbon content. The same results can be obtained if the 18-8 steel contains at least eight times as much columbium as carbon and is given a stabilizing heat treatment after annealing, which consists of holding for two hours at 850-900 degrees Cent. (1560-1650 degrees Fahr.) and air cooling. In fact, steels containing six times as much columbium as carbon are suitable for welded equipment if the operating temperatures are below 300 dedegrees Cent. (570 degrees Fahr.). As shown by Fig. 3, the nickel content of the columbium-bearing steels should be increased to retain the austenitic condition.

The hot workability of these columbium-bearing steels is improved by raising the manganese content from 0.50 to between 1 and 2 per cent. As shown by the data of Table I, increasing the manganese content of these steels to this extent does not lower

their resistance to general corrosion as determined by the boiling 65 per cent nitric acid test.

Physical tests have been made on the steels containing up to 2 per cent manganese. The steels containing between 1 and 2 per cent manganese are equally as strong, ductile, and tough as those having a normal manganese content of about 0.50 per cent.

The columbium-bearing 18-8 steels are used in the form of welding rods. Sufficient columbium can be retained in the weld to impart immunity to corrosive attack in the range from 300 to 800 degrees Cent. (570 to 1470 degrees Fahr.). As previously stated, if

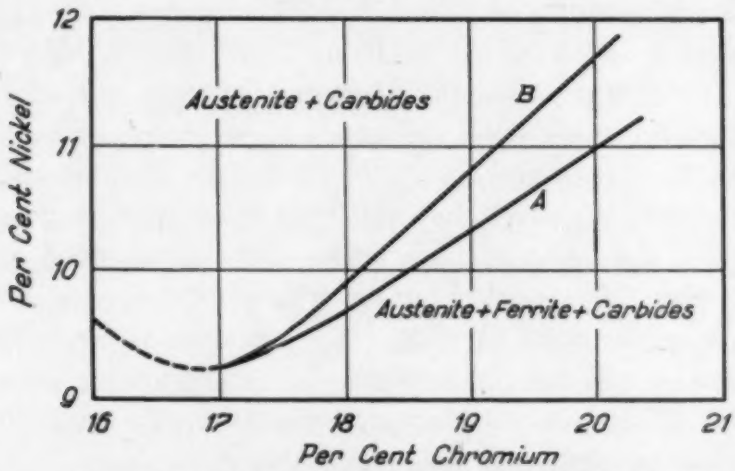


Fig. 3—Structural Diagram for Chromium-Nickel Steels Containing a Maximum of 0.08 Per Cent Carbon and Ten Times as Much Columbium as Carbon. Curve A is for Steels Air-Cooled from 1050 Degrees Cent. Curve B is for Steels Air-Cooled from 1050 Degrees Cent., Held 6 Hours at 650 Degrees Cent. and Air-Cooled.

the structure is to be welded and used at temperatures below 300 degrees Cent. (570 degrees Fahr.) the columbium content can be reduced in low carbon steels to at least six times the carbon content in both the plate and weld metal. The advantage to be gained by using both the larger and smaller percentages of columbium is clearly illustrated by Fig. 4, and it can be stated without reservation that columbium practically eliminates the problem of intergranular corrosion in these most important steels.

Although columbium-bearing 18-8 steels having normal manganese content are satisfactorily welded, there is considerable evidence that generally a somewhat higher than normal manganese content is beneficial. Excellent results have been obtained in the welding of such steels containing 1 to 2 per cent manganese. These welds are sound, ductile, tough, and clean. As shown in Table II.

they have slightly improved resistance to corrosion as determined by the nitric acid test. The silicon content of all the welding rods was kept in the neighborhood of 0.70 per cent to insure a high recovery of columbium in the weld metal. The oxyacetylene welds were made with rods of the composition shown, in plate metal containing 17.84 per cent chromium, 9.74 per cent nickel, 1.16 per cent manganese, 0.41 per cent silicon, 0.08 per cent carbon and 0.85 per cent columbium, while the arc welds were made with similar rods in plates containing 17.91 per cent chromium, 9.43 per cent nickel, 1.70 per cent manganese, 0.49 per cent silicon, 0.08 per cent carbon and 0.82 per cent columbium. In both instances the plate prior to welding was air cooled from 1075 degrees Cent. (1965 degrees Fahr.) and the welds were tested in the as-welded condition. It may be judged from these tests that optimum results, especially in the case of oxyacetylene welding, are secured with about 3 per cent manganese in the welding rod.

Table I
Results of Corrosion Tests on Columbium-bearing 18-8 Steels* Containing up to 2 Per Cent Manganese

Per Cent						Inch penetration per month in boiling 65% nitric acid		
Cr	Ni	Mn	Si	Cb	C	1st 48-hr. period	2nd 48-hr. period	3rd 48-hr. period
18.39	9.02	0.50	0.27	0.72	0.06	0.0010	0.0009	0.0010
18.86	9.45	0.65	0.49	0.74	0.06	0.0010	0.0008	0.0008
17.66	10.10	0.99	0.45	0.54	0.07	0.0010	0.0007	0.0007
17.53	10.47	0.99	0.44	0.87	0.07	0.0011	0.0007	0.0007
17.99	10.01	1.68	0.46	0.84	0.07	0.0011	0.0007	0.0007
19.21	10.55	2.08	0.56	0.96	0.07	0.0010	0.0007	0.0006

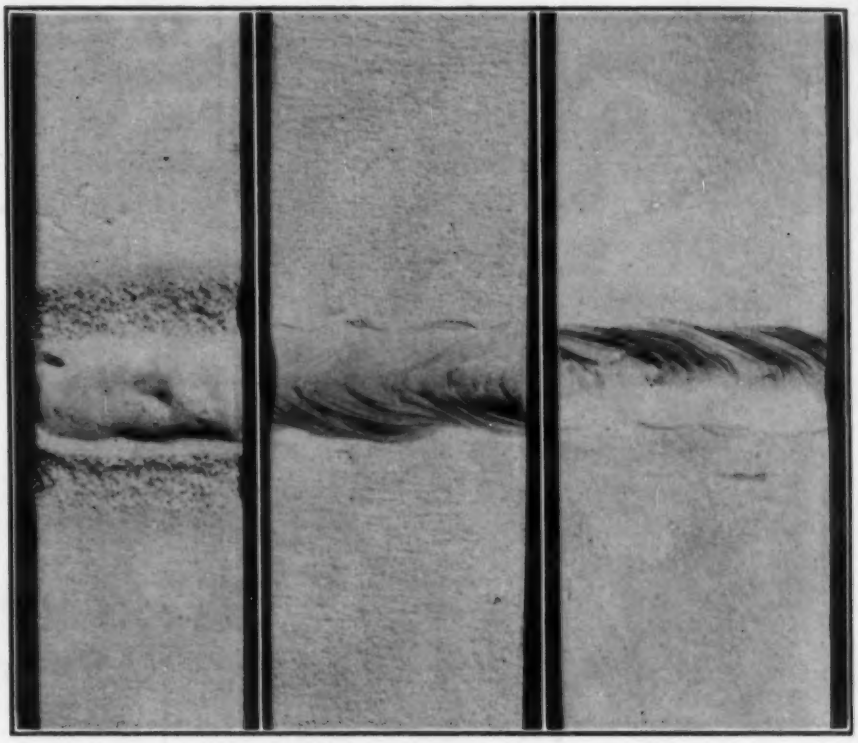
*Tests made on samples taken from ¼-inch plate air cooled from 1075 degrees Cent. (1965 degrees Fahr.)

Table II
Corrosion Tests on Welded Samples of 18-8 Steels Containing Columbium and various Percentages of Manganese

Composition of Welding Rod Per Cent						Thickness of Plate in Inches	Inch Penetration Per Mo. in Boiling 65% Nitric Acid 1st 48 Hr.	2nd 48 Hr.	3rd 48 Hr.	4th 48 Hr.	5th 48 Hr.
Cr	Ni	Si	Mn	C	Cb						
19.68	10.71	0.68	0.60	0.07	0.88	⅛	0.0013	0.0011	0.0015	0.0016	0.0018
19.68	10.71	0.68	0.60	0.07	0.88	½	0.0011	0.0010	0.0011	0.0011	0.0012
19.32	10.70	0.60	2.05	0.08	0.91	⅛	0.0011	0.0009	0.0011	0.0012	0.0012
19.32	10.70	0.60	2.05	0.08	0.91	½	0.0011	0.0009	0.0010	0.0011	0.0010
19.35	9.79	0.69	4.53	0.06	0.96	⅛	0.0011	0.0009	0.0009	0.0011	0.0011
19.35	9.79	0.69	4.53	0.06	0.96	½	0.0011	0.0009	0.0010	0.0011	0.0010

The ½-inch plates were arc welded. The ⅛-inch plates oxyacetylene welded.

Although progress has been made, a complete solution of the problem of local deterioration known as pitting and contact corrosion has not been readily forthcoming. This type of deterioration takes place during exposure to corroding media that ordinarily do not attack the 18-8 steel. It occurs in the form of pits localized at random in different parts of the steel and where contact is made with itself



Cr	18.69	17.65	18.45
Ni	8.72	9.85	9.83
C	0.07	0.07	0.11
Cb	....	0.34	1.11

Fig. 4—Photographs of Plain and Columbium-Bearing 18-8 Steels, Arc Welded and Subjected for Two 84-Hour Periods to a 20 Per Cent Nitric Acid Solution Containing 4 Per Cent Hydrofluoric Acid Held at 60 Degrees Cent. The Welds Were Made in ¼-inch Plate with a Columbium-Bearing 18-8 Steel Rod in the Case of Columbium-Containing Plate, but a Plain 18-8 Steel Rod Was Used on Plain 18-8 Steel Plate. Attack Has Occurred Only in the Latter Plate.

and other materials such as grease, dirt, packing material, and a different metal. Experience has shown that corroding media such as ordinary sea water, brine, weak acid solutions, and some of the common cleaning compounds are likely to cause pitting. Examples of this type of corrosion are shown in Fig. 5.

The cause of pit corrosion is not known, although it is apparent that pickled, ground, or polished surfaces of the steels have local weaknesses, which exist in the annealed condition. The prob-

lem has been difficult to study because of the many variables although a few pertinent observations have been made. Normal inclusions and carbides have not been found to play an important part. Pitting most frequently occurs under relatively weak acid conditions, as strong acid conditions produce general attack. As will be explained later it has been necessary to find corroding media suitable for use in studying the problem. Solutions having pH values between 7 and 4 were found to be satisfactory.

The degree of nobility of the surface of the metal has an important bearing, which in the case of stainless steels indicates that depletion of oxygen is one source of the difficulty. This further indicates that increased rather than decreased nobility is the more practical method of solving the problem. Under such conditions,

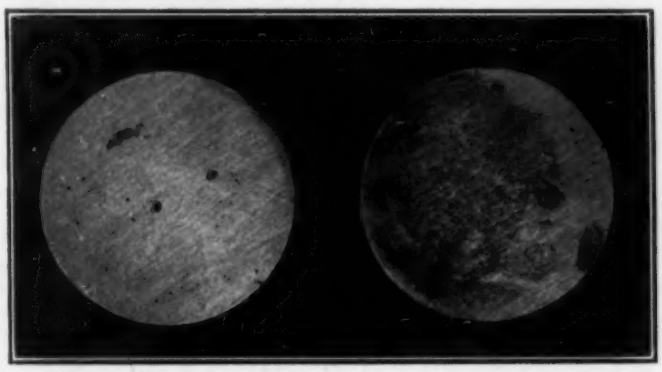


Fig. 5—Photograph at Left Shows the Extent to Which Pitting Occurred in a Low Carbon Wrought 18-8 Steel After Six Months' Exposure to a Spray from a 20 Per Cent Sodium Chloride Solution. Photograph on Right Shows the Contact Corrosion that Occurred Simultaneously on the End of the Sample in Contact with a Glass Plate.

however, nonuniformity of surface with respect to general resistance to corrosion is likely to cause pitting, i.e., when small areas having less resistance to corrosion are adjacent to or near larger areas that have greater resistance to corrosion, the corroding effects on the smaller area are greatly exaggerated. Thus to obtain the best results it is advisable to use a welding rod that gives weld metal with somewhat greater corrosion resistance than that of the parent metal.

Considerable effort has been put forth to eliminate pitting in chromium-nickel steels. Even though, as stated above, the most practical method would consist of increasing instead of decreasing nobility, the latter method has been tried. It was thought that if the chromium content in chromium and chromium-nickel steels was reduced to a point at which general corrosion would proceed at a

slow rate the metal would be substantially free from pitting or contact corrosion. Such steels were more susceptible to the contact corrosion and were not free of pitting. The other method, which consists of improving the nobility of the steels, has been tried with more success. This method, however, has again required modification, necessitating the use of additional elements.

In carrying out these experiments, sea water, 4 per cent sodium chloride solutions, and 10 per cent sodium chloride solutions made with tap water, and containing 0.50 and 5 per cent respectively of ferric chloride, have been employed after much experimentation.

When ordinary sea water remains in a closed vessel for some time its character changes from basic to acid. The pH value decreases from 7.8 to 6.5, and if the vessel is opened or if air is blown through the sea water, it again becomes basic and reaches a pH value between 7 and 8. These facts are not common knowledge because sea water is generally thought of as a basic medium. This seems to explain why the 18-8 steel is pitted by sea water especially in locations that do not have free access to oxygen. When 4 per cent by weight of pure sodium chloride is added to pure water and the solution permitted to remain in the atmosphere for a short time, the solution assumes a pH value of 6.30, which is comparable to the acidity of sea water in a closed system. Thus, this solution has been found suitable for testing susceptibility to pitting over long periods. The 10 per cent sodium chloride solutions containing respectively 0.50 and 5 per cent ferric chloride are more acid and have pH values below 4. They develop pits in the 18-8 steels at a much faster rate than either the sea water or the pure sodium chloride solution and have been successfully used in accelerated testing. All these solutions have been used at room temperature in spray and immersion tests except the sodium chloride solutions containing ferric chloride. These solutions were used only in immersion tests.

The effects of many additional elements on the resistance of chromium-nickel steels to pitting under the above described conditions were studied, and molybdenum was found to greatly improve the steels. It has been found that before substantial resistance to pitting is obtained it is necessary to add at least 2 per cent molybdenum. When the data of Fig. 6 are compared with those of Fig. 5 it is readily noted that the 18-8 steel containing 2.66 per cent molybdenum is considerably more resistant to pitting and contact corrosion than the plain 18-8 steels.

It was realized that a part of the molybdenum added combined with the carbon in the steel; and that if a stronger carbide-forming element than molybdenum were also added, the molybdenum would go into solid solution and exert a beneficial influence. The element found to be most suitable was columbium, and in conjunction with molybdenum encouraging results were secured. These showed that with about 2.50 per cent molybdenum present in an 18 per cent chromium steel containing 14 per cent nickel, 0.10 per cent maximum carbon and 0.50 per cent columbium, relative freedom from pitting under severe conditions was obtained. As shown in Fig. 7, the plain



Fig. 6—Photograph on Left Represents a Sample of Steel Containing 18.73 Per Cent Chromium, 10.59 Per Cent Nickel, 1.98 Per Cent Manganese, 2.66 Per Cent Molybdenum, 0.37 Per Cent Silicon, and 0.07 Per Cent Carbon Exposed for 12 Months to the Spray from a 20 Per Cent Sodium Chloride Solution.

Photograph on Right Represents the End of the Sample that Was in Contact with a Glass Plate. The Sample Did Not Develop Pitting or Contact Corrosion.

18-8 steel sheet was badly pitted after exposure to the sodium chloride solution containing ferric chloride whereas the modified steel containing molybdenum and columbium was free from pits.

Other tests were made to determine the resistance of the modified steel to contact corrosion and the data of Fig. 8 are pertinent. As shown in the figure, the sample tested consists of two parts, a male and female part machined from bar stock, which are screwed together during test. The female part is provided with a flange 0.001 inch thick so that a crack is left between the respective parts. Such a condition might well exist in a riveted or bolt joint. The assembled samples were immersed in a pure 4 per cent sodium chloride solution for several months and inspected from time to time to determine when contact corrosion occurred. Again the plain 18-8 steel was badly pitted in the contact area but the 18-8 steel containing columbium and molybdenum remained practically unaffected.

Tests made on arc welded samples of the columbium- and molybdenum-bearing 18-8 steels to determine the resistance of the welds to pitting gave interesting results. These showed, as revealed by Fig. 9, that the weld metal should be made from metal of a higher degree

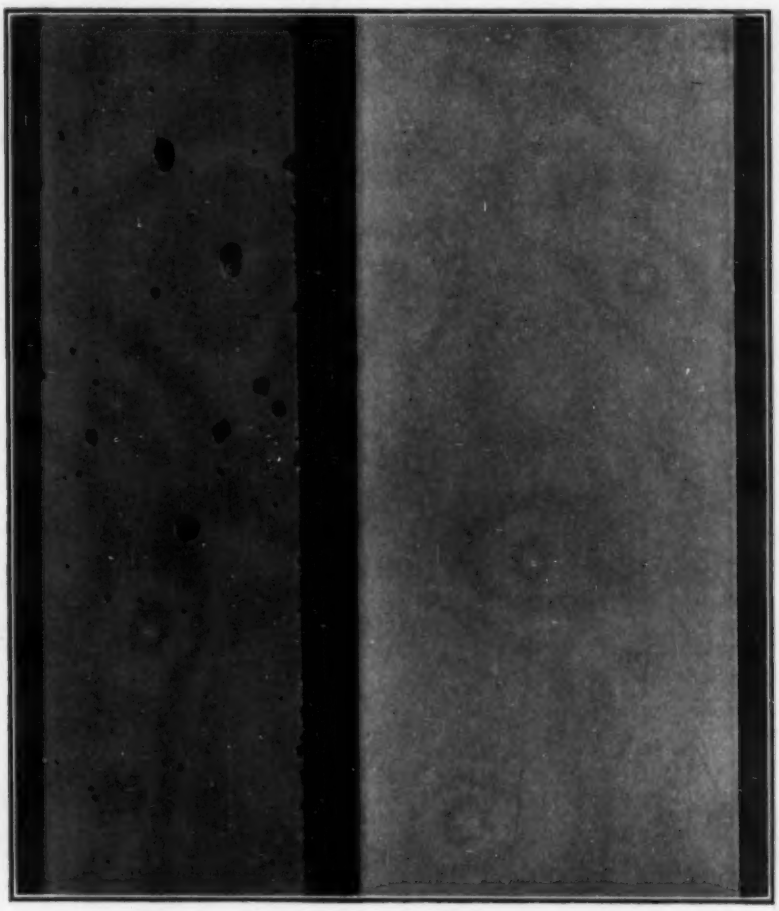


Fig. 7—The $\frac{1}{4}$-Inch Thick Sheet Sample on the Left Represents an Annealed Steel Containing 18.40 Per Cent Chromium, 8.39 Per Cent Nickel, 0.40 Per Cent Manganese, 0.30 Per Cent Silicon, and 0.10 Per Cent Carbon. The Sheet Sample on the Right Was Made from a Steel Containing 18.45 Per Cent Chromium, 10.79 Per Cent Nickel, 1.99 Per Cent Manganese, 0.35 Per Cent Silicon, 2.43 Per Cent Molybdenum, 0.68 Per Cent Columbium, and 0.07 Per Cent Carbon. The Plain 18-8 Steel Sample Was Exposed to a 10 Per Cent NaCl Solution Containing 5 Per Cent $FeCl_3$ at Room Temperature for 18 Hours, While the Modified 18-8 Steel Sample Was Exposed for 65 Hours. The Improvement with Respect to Pitting Obtained in the 18-8 Steel Containing Columbium and Molybdenum Is Quite Evident.

of nobility than the base metal to obtain a welded joint with good resistance to pitting.

These tests have shown definitely that molybdenum and columbium additions to steels of the 18-8 type produce enhanced resistance to both pitting and contact corrosion. The steels containing colum-

bium and molybdenum have several important advantages over those containing only molybdenum. Thick or thin sections can be air-cooled from the annealing temperatures whereas generally it is necessary to quench thick sections of the molybdenum-bearing steels.

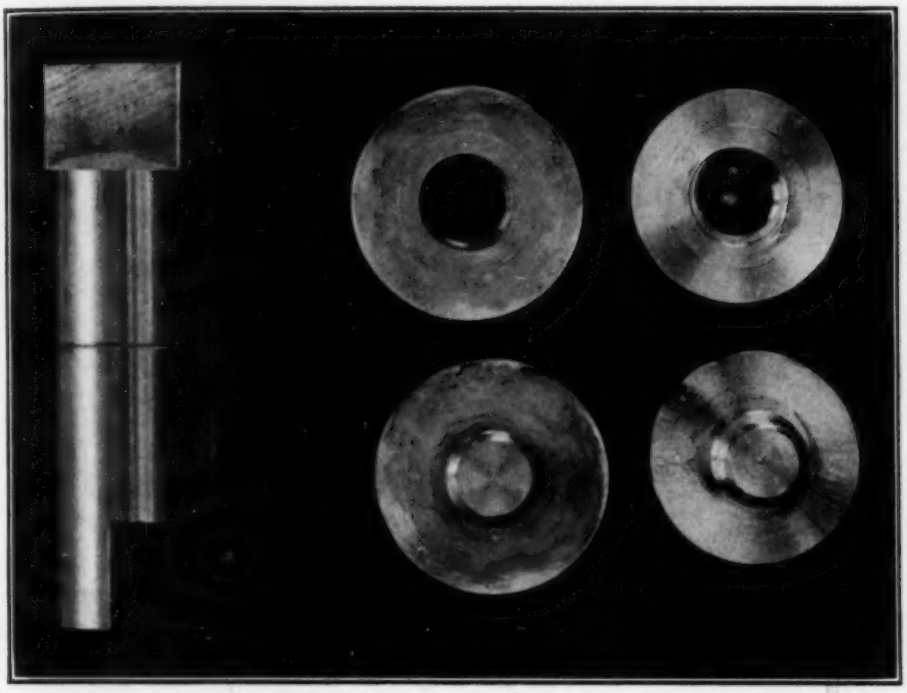


Fig. 8—The Photograph at the Left Shows the Assembled Sample as it is Placed in Test. The Middle Photograph Shows the Condition of the Adjacent Surfaces of a Steel Containing 19.89 Per Cent Chromium, 9.40 Per Cent Nickel, and 0.08 Per Cent Carbon After 12 Months' Exposure to a Pure 4 Per Cent NaCl Solution at Room Temperature. The Surfaces of This Steel Were Badly Corroded, Although Those of the 18.10 Per Cent Chromium, 10.50 Per Cent Nickel, 0.58 Per Cent Columbium and 1.99 Per Cent Molybdenum Steel at the Right Were Substantially Free of Attack. The Samples in Both Instances Were Prepared from Annealed Steels.

The steels are suitable for welding and do not require heat treatment to prevent deterioration in the weld or zones adjacent to the welds. They are free of susceptibility to intergranular corrosion and have a high degree of resistance to general corrosion but if held for long periods at 650 degrees Cent. they suffer a loss in this property.

Silicon, manganese, copper, tungsten, cobalt, vanadium and selenium have been added to either the chromium or chromium-nickel steels or both. Time will not permit a full discussion, but the effects of the different metals will be briefly mentioned. Silicon helps oxidation resistance but increases the grain size of both types of steels. Manganese improves hot working characteristics, and weldability, and assists austenite formation. It has been used to replace a portion

of the nickel in the austenitic steels. Copper is in some cases added for increased corrosion resistance; tungsten for increased strength at elevated temperatures; cobalt, molybdenum, and vanadium in the high chromium die steels for reduced grain size and enhanced harden-

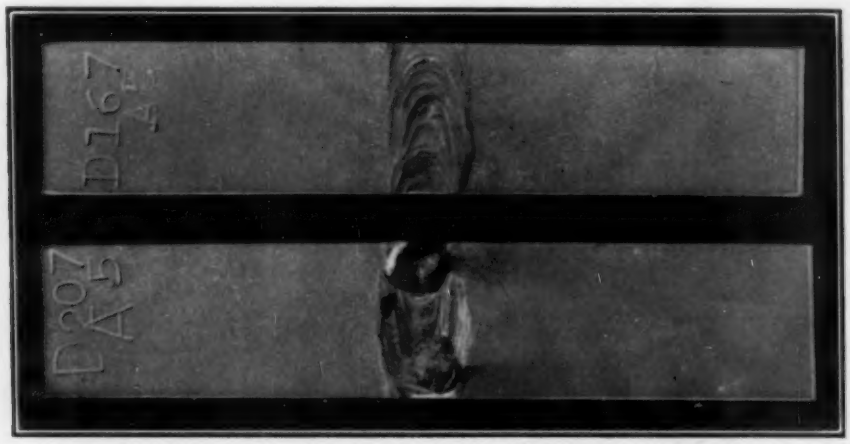


Fig. 9—These Photographs Show the Condition of Welds Made in Annealed ⅛-Inch Thick Plate of a Steel Containing 19.02 Per Cent Chromium, 12.07 Per Cent Nickel, 1.99 Per Cent Manganese, 3.06 Per Cent Molybdenum, 0.83 Per Cent Columbium and 0.09 Per Cent Carbon. The Samples Were Exposed in the Welded Condition to a 10 Per Cent NaCl Solution Containing 5 Per Cent $FeCl_3$ at Room Temperature for 65 Hours. The Photograph on the Bottom Shows the Condition of the Weld Made with Rod of the Same Composition as the Plate. While the Plate is Satisfactory, the Weld Metal is Pitted. The Photograph on the Top Shows the Condition of the Weld Made with a Steel Containing 22.41 Per Cent Chromium, 13.93 Per Cent Nickel, 2.05 Per Cent Manganese, 0.84 Per Cent Columbium, 2.72 Per Cent Molybdenum, and 0.08 Per Cent Carbon. In This Instance Both the Weld and Plate Are Free of Pitting.

ing ability; and finally selenium for improved machinability in the chromium-nickel steels.

As earlier stated, the purpose of this paper has been to discuss the effects of some of the important additions to stainless steels. More detailed information has been given on certain of the additions. The discussion has been presented in this manner so that the effects of the more recent additions could be described sufficiently to show justification for their incorporation in the stainless steels.

An attempt has been made to convey the idea that progress has been made in solving difficult problems through modifying the analysis of stainless steels and to leave the thought that further modification of the steels may be necessary to meet more exacting requirements. Stainless steels have already served well, and their use in general must be economically successful to broaden the field of application—the chief reason for modification of these almost indispensable steels.

DISCUSSION

Written Discussion: By E. H. Davidson, manager, Stainless Steel Bureau, Carnegie-Illinois Steel Corp., Pittsburgh.

Mr. Franks' paper is a welcome addition to the subject and the reasons set forth for the additions discussed are very helpful. However, there are some phases of the paper which may be commented upon, largely with the thought of stimulating further work.

Based on the extensive work that has been done on the titanium-bearing 18-8 steels, it is considered that when speaking of actual carbon analyses up to 0.07 per cent, titanium to the extent of four times the carbon content is sufficient to stabilize the carbide and, accordingly exception is taken to the six times minimum given by the author.

In the case of columbium-bearing 18-8 steels, it is quite true that the increased manganese coupled with a better balanced ratio of nickel to chromium has produced marked improvement in hot working properties. However, even with these advantages, the hot working characteristics with a minimum columbium content of 10 × carbon are not comparable to the straight 18-8 or the 18-8 titanium-bearing grades.

It might be mentioned that we somewhat question the usual columbium specification of 10 × minimum actual carbon content which results in columbium running around 0.70 per cent or higher due to the difficulty of working to carbons below 0.06 or 0.07 per cent. We have found from both experimental laboratory heats and production melts that hot working difficulties are sometimes encountered when the columbium content exceeds 0.55 per cent. We believe that for many applications involving sensitizing periods no longer than one hour, such as the heating of the base metal incident to welding. a minimum columbium content of 6 × the carbon would be sufficient. For severe service, however, and particularly when the service temperature is within the carbide precipitation range, a Cb/c ratio of 8 is recommended if the material contains not over 0.08 per cent carbon and is stabilized, or a ratio of 11 without stabilizing.

In line with the author's work on this subject, it is believed that this work could be carried further to appreciably lower these detrimental properties. Possibly the manganese may be raised still higher and some other adjustment in analysis be made either by additional element or variation in present constituents. Obviously any such change should be made with full consideration for the corrosion resistance and all other pertinent properties.

With reference to the general remarks pertaining to the addition of nitrogen to the high chromium type, we are in accord that the nitrogen additions have been beneficial to the hot working properties of the material. We would be interested to hear of any experiences the author has had in relation to the effect carbon or other constituents may have on this property.

Written Discussion: By H. L. Maxwell, technical division, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

This paper is a valuable addition to the literature on stainless steels and, it is believed, will be of substantial help to users of stainless alloys in developing and prescribing equipment applications.

The successful use of columbium as a stabilizing element in low carbon 18-8 material, as developed in this paper by the author, finds ready application in the fabrication of plant scale equipment. The author points out that *Cb* ratios of 10, 8 and 6 may be used under specific C service conditions and still give relative immunity from intergranular attack in service. Our experience would indicate that ratios in the range of 10 are preferred. This statement is based on accelerated laboratory corrosion tests, inasmuch as columbium modified 18-8 has not been installed in plant scale equipment long enough to develop what may be termed a typical plant failure. There is, however, no doubt, to judge by extensive experimental work and some plant scale equipment, that columbium stabilized 18-8 may be used economically in fabricating certain equipment which it is impractical or not economical to give the regular heat treatment after fabrication.

In reference to the corrosion rates on columbium stabilized 18-8 with varying amounts of manganese, the discussor wishes to add that these corrosion rates check his unpublished values within close limits. In making corrosion tests in boiling 65 per cent nitric acid it is our standard practice to continue the tests through five 48-hour periods.

The author is to be commended on this paper. It contains new and useful information and may well be made the subject of study by those concerned with stainless steels and their uses.

Written Discussion: By F. L. LaQue, development and research division, International Nickel Co., Inc., 67 Wall Street, New York City.

Mr. Franks in his excellent summary of reasons for adding special elements to the common stainless steels, furnishes ample proof that the complications in composition that result from such alloy additions are well justified by the results obtained.

In his discussion of the chromium ferritic steels, Mr. Franks evidently overlooked the 18 per cent chromium steel containing about 2 per cent nickel. The principal effect of this amount of nickel is to make the alloy amenable to hardening by heat treatment. The alloy is usually specified to contain a maximum of 0.25 per cent carbon. A typical specimen having a hardness of about 220 Brinell in the as-rolled condition was heat treated to a hardness of about 350 Brinell by quenching in oil from 1750 degrees Fahr. It was then drawn back to about 290 Brinell by tempering at 1200 degrees Fahr. This alloy has been used to a considerable extent, especially abroad, as a replacement of plain chromium steels containing from 12 to 18 per cent chromium. Its corrosion resistance is superior to that of the hardenable steels of lower chromium content, and it is both stronger and more corrosion resistant than the plain chromium steels having the same chromium content. Its corrosion resistance is, of course, distinctly inferior to that of the austenitic stainless steels.

A reported advantage of the 18-2 alloy over the plain chromium steels is a lesser susceptibility to accelerated corrosion when used in galvanic content with bronze in such media as sea water.

Typical applications include pump rods and shafts, valve trim, structural members in aircraft, and moulds for soap, plastics, etc.

It may be noted, in passing, that relatively small amounts of nickel—

up to 2 per cent—are regularly used in chromium steels to increase the hardenability of the heat treatable alloys and to improve the ductility, especially in the cold-worked condition, of those that are not heat treated. The alloys containing nickel are also easier to handle in the mill. A useful effect of nickel in all these alloys is to improve their resistance to corrosion.

In his discussion of the phenomena of pitting and contact corrosion of stainless steels in certain environments, Mr. Franks quite properly associates these occurrences with variations from point to point in the degree of nobility of the alloy surfaces.

Unfortunately, as Mr. Franks pointed out, it seems to be impractical to modify these alloys of iron in the direction of lowering their apparent nobility to a controlled extent so that uniform corrosion will proceed at a satisfactory low rate and local corrosion or pitting will be avoided. The alternative modification in the direction of increased nobility suggested by Mr. Franks as being more promising should include increases in the nobility of the alloy itself, as well as of the protective surface films which it may develop. Any improvement in apparent nobility that serves principally to decrease the probability of local attack without, at the same time, reducing the intensity of corrosion at points where the protective film may break down, will fail to provide a satisfactory foolproof alloy. Any modification which merely reduces the number of points of attack may be more harmful than helpful, since it has been observed that the fewer the pits per unit area, the deeper they are likely to be.

Fortunately, there is considerable evidence to indicate that real progress is being made in improving both the alloys and the characteristics of the surface films which they develop. This seems to be especially the case in connection with the weak acid solutions, common cleaning compounds, and some brine solutions mentioned by Mr. Franks as having been troublesome.

In the case of sea water, it appears that it is still difficult to secure a stainless steel that is free from local corrosion under all conditions.

In fact, we still seem to lack an adequate diagnosis of the disease we are trying to cure. There are plausible explanations of the mechanism of pitting after it starts, but there is, as yet, no satisfactory reason why it should start at any particular point in the first place.

It has been suggested that ferric chloride resulting from previous corrosion of some ferrous material may be the initiating agent. However, W. A. Wesley and C. H. Lindsley have found[1] that ferric chloride is practically insoluble in sea water unless its acidity has been increased well above any limit likely to be encountered under natural conditions.

Mr. Franks reported his observation that a sample of naturally alkaline sea water became slightly acid when kept in a closed vessel, and then became alkaline again when it was subsequently aerated. He has suggested that this development of acidity in closed spaces may be responsible for the development of local attack. Mr. Franks did not suggest what might be the nature of the chemical changes associated with these variations in acidity. It is conceivable that the increase in acidity observed by Mr. Franks when a sample

[1] *Metals and Alloys*, December 1937.

of sea water was kept in a closed vessel may have been due to the decomposition of organisms in the water. It is also possible that the decomposition products might include carbon dioxide, hydrogen sulfide, or other acidic gases and that the effect of the subsequent aeration would be to sweep out these gases and thereby restore the normal alkalinity.

The equilibrium pH of natural sea water is maintained by inter-reaction between carbonates and bicarbonates in solution, carbonaceous organisms and plant life living in the water, and carbon dioxide in the atmosphere. In his book on the Chemistry and Physics of Sea Water, H. W. Harvey[2] presented data to indicate that the equilibrium pH of natural sea water is about 8.1 or 8.2 and that, unlike synthetic sodium chloride solutions, natural sea water is well buffered by the bicarbonate and other salts, as well as by the living matter present.

Consequently, it does not seem probable to this writer that the pH of natural sea water will be lowered sufficiently, merely by excluding air, to bring about local attack of stainless steels. This is especially not likely to be the case under, or in the immediate vicinity of, alkaline carbonaceous matter, such as barnacle shells, where pitting has been frequently observed. Local corrosion under barnacles, especially after they have died, is quite probably accelerated by sulphur compounds released from the decomposing organisms.

One of the principal difficulties in the development of alloys resistant to sea water is to find a laboratory testing procedure by means of which the true behavior of a material in natural sea water can be predicted. The problem is complicated by the fact that investigators both in this country and abroad have found that both living and dead organisms, including bacteria, may have a profound effect on the characteristics of sea water as a corrosive.

Tests in simple sodium chloride solutions, synthetic sea water, salt sprays, or such more violently corrosive media as ferric chloride, may serve to weed out the obviously bad alloys from the probably good ones, but it still seems to be necessary to check these laboratory tests by exposure of specimens, or by the actual use of the alloys, in sea water under natural conditions.

The importance of this fact is well illustrated by some data that became available after Mr. Franks' manuscript was sent in for publication.

For inclusion in some tests in natural sea water being carried out by the writer and his associates, Mr. Franks kindly submitted specimens of alloys having practically the same composition as those represented by Figs. 6 and 7 of his paper, and which in various laboratory tests, to which he subjected them, were remarkably free from pitting and contact corrosion. Nevertheless, after exposure for from 2 to 2½ years in natural sea water, these specimens were severely pitted. The alloy containing about 19 per cent chromium, 10 per cent nickel, and 2¾ per cent molybdenum was pitted to a maximum depth of 0.06 inches, while the alloy having similar chromium, nickel and molybdenum contents, plus about ½ per cent columbium, was even more severely pitted to a maximum depth of 0.21 inches.

In spite of the disappointing performance of these particular specimens, there is considerable evidence to indicate the value of molybdenum additions

[2]Cambridge University Press, Fetter Lane, London, 1928.

Table I

Results of Plant Corrosion Tests of Stainless Steels in Various Media

Corrosive	Process Unit	Temp. Degrees Fahr.	Duration of Test, Hours	Corrosion Rate in Mg./Sq.Dm./Day				
				Type 302 18 Cr 8 Ni 0.08-0.20 C	Type 304 18 Cr 8 Ni 0.08 Max. C	Type 316 16-18 Cr 8-14 Ni 2- 3 Mo 0.10 Max. C	Type 321 18 Cr 8 Ni + Ti	Type 347 18 Cr 8 Ni + Cb
Mixed fatty oils + H_2SO_4	Twitchel kettle	212	1032	111	123	29	...	...
Cottonseed fatty acids	Flash zone of still	530	1212	184	237	0.3	...	...
Mixed oleic and stearic acids	Still, below liquid level	440	504	86	103	...	112	...
Mixed oleic and stearic acids	Heat exchanger	600	100	...	1070	1	...	1200
Glacial acetic acid	Topping column on still	Boil	504	335	168	6	282	232
Amyl alcohol + 40% acetic acid and 0.2% H_2SO_4	Esterification	255	....	...	27	18	...	...
90% formic acid	Still-below liquid level	212	192	0.7	0.2	0.9	0.7	...
90% formic acid	Still-in vapor space	212	648	467	143	10	127	...
Lactic acid 10 to 50%	In evaporator	125	1680	9	14	3	5	...
Benzol xylol toluol + SO_2 + NH_4OH	Condenser	175 to 250	1776	...	34	7	...	...
Ethylene diamine hydrochloride	Autoclave	230 to 320	16	7570	18200	15	...	...
1.24 s.g. ammonium sulfate with 8.4 g.p.l. H_2SO_4, 0.9 g.p.l. SO_2	Tank	155	144	3443	3464	0.4	4036	3881
Mixture of 5% HF, 5% H_2SO_4, 10% H_2SO_4 saturated with air	Lab. test	120	40	2160	...	1048	...	...
		240	120	>6000	...	47	...	...
70% phosphoric acid	Storage Tank	230	432	103	108	117	...	...
Tetrachloride of tin + Cl	Still, below liquid level							

in reducing susceptibility to serious pitting. This subject was discussed in some detail by H. A. Smith in a paper that appeared in the June 1938 issue of *Metal Progress*. Although the ultimate has not yet been reached, substantial progress has been made and, no doubt, will continue to be made.

During the past few years the writer has exposed a variety of stainless steels to a number of corrosives encountered in several chemical processes. All of these tests were made under actual plant conditions, and, although the data have limited general application, a selection from them has been made to illustrate the effects of such elements as carbon, molybdenum, titanium and columbium on general corrosion resistance as distinct from pitting or intergranular attack. These data are given in Table I.

It appears from these data that molybdenum has a specific, and, in many cases, a surprisingly powerful and beneficial effect in certain environments, whereas the usefulness of columbium and titanium is most likely to be confined to the avoidance of intergranular attack, as described by Mr. Franks. It would also appear that the effect of carbon, per se, is not as important as has been generally believed.

Written Discussion: By Ernest H. Wyche, research laboratory, United States Steel Corporation, Kearny, N. J.

Mr. Franks has given a good discussion of this phase of stainless steel and he has presented it in a manner which is not too technical, thereby enabling him to reach the ever-increasing number of users of these steels. In the discussion of the addition agents columbium and titanium, there is one point which, we believe, might be stressed more, and that is the essential similarity in behavior of these two elements, when comparable amounts are present, as inhibitors of intergranular corrosion in the austenitic chromium-nickel steels. Thus, according to our experience, to secure equal protection it is necessary to have about twice as much columbium as titanium, other things being equal; this we interpret in the sense that one atom of columbium (atomic weight 93) is equivalent, so far as carbide formation is concerned, to one atom of titanium (atomic weight 48).

Mr. Franks states "when titanium is used it must be present to the extent of at least six times the carbon content, and the steel must be given a stabilizing heat treatment . . . ." This statement should, in our opinion, be modified because both laboratory data and service tests, extending over a number of years, have shown that, for mild service, stabilization is not needed provided that the proper amount of titanium relative to the carbon content is present. Bain, Aborn and Rutherford[a] showed that when Ti/(C — 0.02) is 5.5, this ratio suffices to prevent intergranular attack on metal which had received no stabilizing treatment and had been exposed for 16 hours to sensitizing conditions. For example, with 0.07 per cent carbon, which is the maximum carbon content now customary in austenitic stainless steels to be used where intergranular corrosion may occur, the minimum titanium requirement is 5.5 (0.07 — 0.02) = 0.28 per cent. Actually this 16-hour exposure is at least as severe as is encountered in a large number of applications, for instance, where the

[a]E. C. Bain, R. H. Aborn and J. J. B. Rutherford, "The Nature and Prevention of Intergranular Corrosion in Austenitic Stainless Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 21, p. 481 (1933). As a safe working rule for commercial usage the 5.5 factor in this ratio was recommended by Bain and co-workers to be raised to 6.

metal is welded and stress relieved, (provided that these processes require no longer than 16 hours in the range of sensitizing temperatures) and is to be used at ordinary temperatures.

We believe, however, that the stabilizing heat treatment, though not always necessary, is advisable regardless of whether titanium or columbium in comparable quantities have been added, as an assurance against intergranular corrosion under the severer condition of exposure.

MERRILL A. SCHEIL:[4] Mr. Franks has presented a splendid paper on alloy additions. After reading over this paper I had one thought in connection with the nitric acid corrosion data given in Table II. It is apparent that the author has subjected arc welded samples to the hot nitric acid test, and that these have shown a remarkable corrosion resistance. Since the author has raised the point of the relative corrodability of arc weld metal and plate material I believe that more conclusive tests could be shown. The data should state how much of the sample was weld metal. The conclusions arrived at would be more convincing if the author had shown the corrosion rates on all weld metal samples containing various percentages of manganese. In this connection it would be more valuable if the manganese content of the weld metals were given as well as the manganese content of the weldrod. It would be especially interesting if the author would report on corrosion tests of multi-pass arc welds produced with the higher manganese weldrods.

In connection with Fig. 3, which I find very interesting, I believe Mr. Franks should tell us the manganese contents of the different alloys used.

Author's Reply

Dr. Maxwell's comments on the data given in the paper are greatly appreciated. His company has used large tonnages of the 18-8 steels, and it is felt that his opinion concerning columbium-bearing 18-8 steels will be of help to others in properly using the steels in the chemical industry. It is also pleasing to learn that unpublished nitric acid data obtained by Dr. Maxwell confirm those shown in the paper for columbium-bearing steels containing various percentages of manganese.

Mr. Davidson's remarks are pertinent, particularly in connection with the improved hot workability of the columbium-bearing 18-8 steels having an increased manganese content with a suitable ratio of nickel to chromium. We believe that most of the difficulty Mr. Davidson refers to in hot working the 18-8 steels containing ten times as much columbium as carbon has been due to unbalanced analyses. It is a fact that during the last two years considerable quantities of the steels have been fabricated into wrought products without encountering serious difficulty, and the opinion may be expressed that the steels are readily hot-worked when proper adjustment is made in the analysis. Work has already been started on the effects of more than 2 per cent manganese on the properties of the columbium-bearing 18-8 steels.

Mr. Davidson takes exception to the statement that in order to obtain complete immunity to intergranular corrosion the 18-8 steels should contain at least six times as much titanium as carbon. The reason for making this state-

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[4]Research metallurgist, A. O. Smith Corp., Milwaukee.

ment is based on results obtained on commercial titanium-bearing 18-8 steels. For instance an 18-8 steel containing 0.09 per cent carbon and 0.43 per cent titanium exhibited susceptibility to intergranular attack after holding for 1000 hours in the range 480 to 580 degrees Cent. This steel was previously air cooled from 1150 degrees Cent., held four hours at 850 degrees Cent. and air cooled. It was found in a similar test on an 18-8 steel containing 0.06 per cent carbon and 0.40 per cent titanium that the metal was free of susceptibility to intergranular attack after heat treating in the same manner.

It is gratifying to receive Mr. Davidson's report on the beneficial effects of nitrogen on the hot workability of the plain high chromium steels.

Mr. Wyche is correct in stating that more columbium than titanium is needed in stabilizing the 18-8 steels. This, however, is no handicap because better recoveries of columbium are obtained in melting the steels. The differences between the effects of columbium and titanium have been described in the paper and need not again be repeated. Mr. Wyche expresses the opinion that the stabilizing heat treatment is advisable whenever titanium or columbium is used to impart freedom from intergranular attack under severe conditions. This is true in the case of titanium, but the fact is that the columbium-bearing 18-8 steels employed in industry are not generally given a stabilizing heat treatment.

It can be stated in answer to Mr. Scheil's comments that the welded samples were about 3 inches long by 1 inch wide with a welding bead of normal thickness. The samples were prepared by multiple-pass welds, i.e., five beads were deposited in preparing the ½ inch thick arc welded samples. The manganese content of the steels described by Fig. 3 was between 1 and 2 per cent.

Mr. LaQue's discussion is unquestionably a valuable addition to the paper. The increase in strength obtainable in the 12 to 18 per cent chromium steels by the addition of 1 to 2 per cent nickel should have been stressed. There are three steels in this category which are: 12 per cent chromium and 2 per cent nickel, 18 per cent chromium and 2 per cent nickel, and 16 per cent chromium and 1 per cent nickel. The first-mentioned steel is used for springs, while the other two are primarily for aircraft construction. It has not been our experience that these small percentages of nickel markedly increase corrosion resistance. They are added chiefly to obtain improved hardening characteristics in the low carbon steels.

Mr. LaQue's comments on the subject of pitting are of considerable interest. He cites work done by W. A. Wesley and C. H. Lindsley which showed that ferric chloride was practically insoluble in sea water unless the acidity was increased well above the limit likely to be encountered under natural conditions. This is hardly sufficient to warrant the statement that ferric chloride does not play an important part in the pitting of the 18-8 steels. Large quantities of ferric chloride would not have to go into solution to cause pitting as extremely small percentages could initiate the action. Our experience has been that in every instance when pitting has occurred in salt solution iron salts were formed, and when pitting was absent iron salts were apparently not formed.

Mr. LaQue cites the results of tests made on samples of 18-8 steels containing molybdenum, and 18-8 steels containing both molybdenum and colum-

bium in which more pitting occurred on the steels containing columbium. He fails to state, however, that in the same tests the columbium-bearing steels exhibited greater freedom from contact corrosion. The paper does not claim that laboratory tests can be used to conclude definitely that steels of this type will be free of pitting in service. It only points out that certain steels are more resistant to pitting than others, and laboratory tests are certainly adequate for this purpose. Incidentally Mr. LaQue recently supplied us with a sample of 18-8 steel containing molybdenum that had been tested off the coast of North Carolina for a period of about two years, and was found to be quite resistant to pitting.

It must be emphasized in closing, that the purpose of the paper was to show the effort being made to render the stainless steels more serviceable. The value of the steels should not be underestimated because of this frank discussion in regard to the relatively few difficulties that have been met with in using them. Their few weaknesses must be recognized as in the application of other materials of construction, so that successful use can be made of their valuable properties.

EFFECT OF H_2 ON BODY-CENTERED–FACE-CENTERED TRANSITION IN IRON

By C. B. Post, R. E. Lake, and W. R. Ham

Abstract

Hydrogen in solution in iron causes a small but measurable lowering of the body-centered–face-centered transition temperature. Changing the hydrogen pressure on the entering side of a relatively pure iron sheet from 74 cm. to 18 cm. of mercury, and keeping a pressure of not more than 0.0030 cm. on the exit side, raises the transition point, as measured by the diffusion method, approximately 1 degree Cent. Hence, about 2 degrees Cent. should be added to this transition point as obtained by hydrogen diffusion methods, but approximately 4 degrees Cent. should be added when this transition is obtained under conditions such that all sides of the iron sample are exposed to hydrogen at atmospheric pressure. Theoretical considerations lead to the same conclusion. The transition temperature determined by Wells, Ackley and Mehl therefore needs negligible correction for hydrogen concentration, but that of Roberts and Davey should have 4 degrees Cent. added.

A technique is also described which enables one to obtain a completely "steady state" at the body-centered–face-centered transition. Hysteresis can be almost entirely eliminated by working back and forth through the transition, using a small temperature range, and allowing the sample to come to complete equilibrium at each temperature.

DURING the course of experiments on the diffusion of hydrogen through metals at high temperatures, the writers have obtained data concerning the effect of hydrogen concentration on the alpha-gamma transition in iron. This information may be of interest to metallurgists, especially those needing the most accurate temperature value of this transition in pure iron.

The samples of pure iron prepared in the past for examination of the body-centered–face-centered region appear to have been obtained from two main sources. In general, a compound of iron is

Of the authors, C. B. Post and R. E. Lake are members of the Department of Physics and W. R. Ham is Head of Department of Physics, School of Chemistry and Physics, Pennsylvania State College, State College, Pa. Manuscript received January 4, 1938.

decomposed, or transformed, chemically under such conditions that the danger of contamination by other metals is minimized. This compound is often $Fe_2(CO)_3$ or Fe_2O_3. The method using the former is based upon the elimination of CO by the application of heat; the resulting iron is formed into sheets about ⅛ inch thick, these sheets obviously containing some carbon. The carbon can be almost entirely eliminated by prolonged heating in a hydrogen atmosphere at about 1000 to 1100 degrees Cent. (1830 to 2010 degrees Fahr.). The oxide preparation, Fe_2O_3, is reduced in a hydrogen atmosphere. The transition point of the oxide-prepared iron has been determined by Roberts and Davey (loc. cit.) when the iron was in equilibrium with a surrounding hydrogen atmosphere.

However, recent experimenters[1, 3] have used the carbonyl type iron more widely than that type formed by the reduction of the oxide[2]. The residual carbon is generally removed by the above mentioned treatment with hydrogen, and after such decarburizing treatment the measurements have sometimes been made in an inert atmosphere such as argon or helium. The amount of residual hydrogen present in the sample has generally not been ascertained.

It is easy to obtain reproducible results on the rate of diffusion of hydrogen through a particular sample of iron in the body-centered–face-centered region, and equally easy to change the hydrogen pressure (and hence the concentration) on the entering side. The concentration on the exit side can be conveniently maintained exceedingly small. Consequently, it seemed worthwhile to examine the behavior of the body-centered–face-centered transition as the hydrogen concentration in the sample was varied.

Experimental Results

A complete description of the necessary apparatus for diffusion studies as developed in this laboratory can be found in previous publications[3, 4]. The first observation worth calling attention to is the technique developed for studying "steady state" conditions at, and in the neighborhood of, allotropic transformations. This technique was the result of concern felt over the lack of agreement be-

[1]Wells, Ackley and Mehl, Transactions, American Society for Metals, Vol. 24, 1936, p. 46.

[2]Roberts and Davey, *Metals and Alloys*, Vol. 1, No. 14, 1930, p. 1.

[3]W. R. Ham, Transactions, American Society for Metals, Vol. 25, 1937, p. 536-564.

[4]C. B. Post and W. R. Ham, *Journal* of Chemical Physics, Vol. 5, 1937, p. 913-919.

tween dilatometric and diffusion studies on the question of hysteresis at the A_3 point in pure iron. In the previously mentioned publication by Ham[3] it was shown that quite a hysteresis effect is to be noted at the A_3 point, and this in the face of the experimental fact that diffusion rates can be obtained under "steady state" conditions, i.e., a temperature can be held indefinitely by this method until the diffusion rate reaches a steady value. On the other hand, Wells, Ackley and Mehl[1], in a precision dilatometric study of A_3 in pure

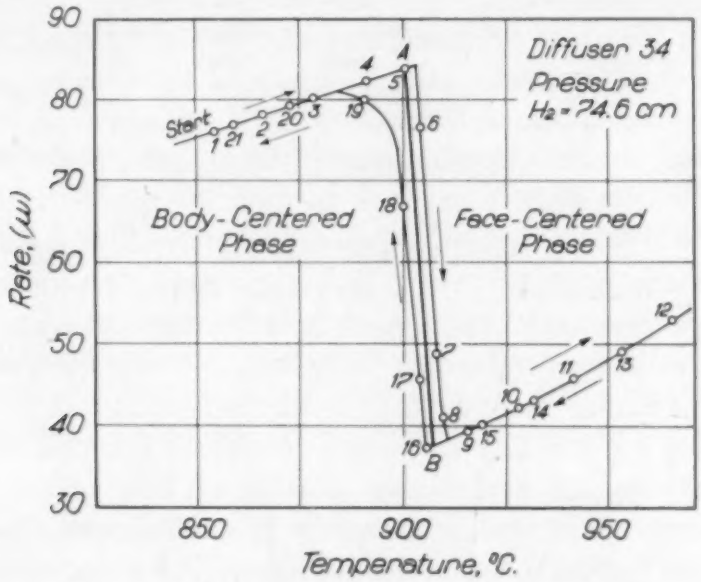


Fig. 1—Hysteresis at A_3 in Carbonyl "Mehl" Iron.

carbonyl iron, showed quite clearly that an extrapolation to zero rate of cooling, or heating, gave little or no hysteresis for this transition.

On going back through our experimental data we found that Ham followed quite a definite procedure in obtaining the data shown in his paper[3] which represented a summary of hydrogen diffusion work along these lines to the date of publication. This procedure was characterized by the fact that the observations about A_3 were always begun at a temperature 50 to 75 degrees above or below the transformation point and continued to about the same distance on the other side.

More recently, the hydrogen diffusion technique for studying these allotropic modifications has been changed to match that of physico-chemical practice in studying melting or freezing points. To illustrate, consider Fig. 1. The observations were started at 800 degrees Cent. (1470 degrees Fahr.) and the diffusion rate measured

in steps of 2 to 3 degrees Cent., by holding the sample at any particular temperature until the diffusion rate reached a steady value. After passing through the Ac_3 region, readings were continued until a temperature of 960 degrees Cent. (1760 degrees Fahr.) was reached. The rates were similarly read as the temperature was lowered through the Ar_3 region. Thus, Fig. 1 shows the type of hysteresis observed by Ham.

Now consider Fig. 2. Here we start as before at 960 degrees Cent. (1760 degrees Fahr.) and lower the temperature gradually until the Ar_3 region is reached. We now go about 5 degrees below

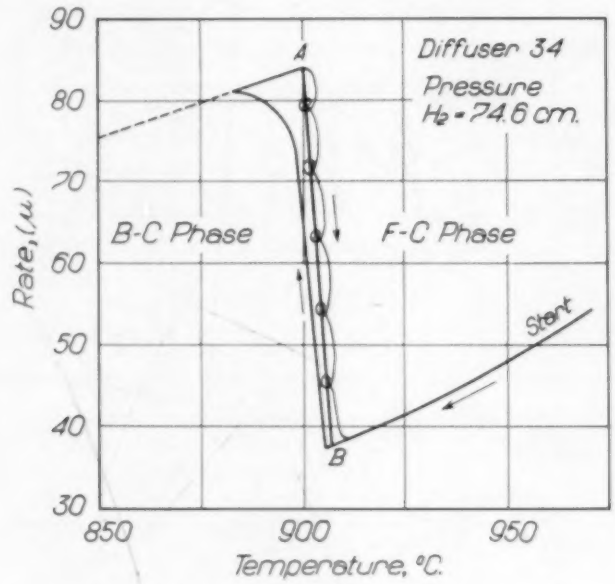


Fig. 2—Equilibrium Conditions at A_3 in Carbonyl "Mehl" Iron (Heavy line AB).

Ar_3 and immediately start taking readings as the temperature is raised. When the rate begins to fall from the high body-centered rate to the lower face-centered rate, we lower the temperature slightly and observe whether the rate goes up or down. By suitable manipulation of the thermostatic controls, a point approximately in the center can be found where the rate goes neither up nor down. This, obviously, is a true equilibrium point because of the fact that we are giving the phases ample freedom for transformation, i.e., the crystals are amply "seeded" with both types of phases. This same procedure can be followed to find an equilibrium point somewhat nearer the face-centered, or the body-centered, phase. Thus the heavy line drawn in Fig. 2 represents the region in which both face-centered and body-centered iron can co-exist. The edges of the

diffusion disks are slightly contaminated with gold (from the gold weld), consequently the rim transforms at a different temperature than the pure iron in the center. This causes the end points of the transformation to be masked and the effect is manifested by the gradual appearance of the end points, as shown in Fig. 1, rather than the ideal abrupt appearance which one might expect.

The experimental determination of the effect of hydrogen on the A_3 point was obtained by varying the entering pressure of hydro-

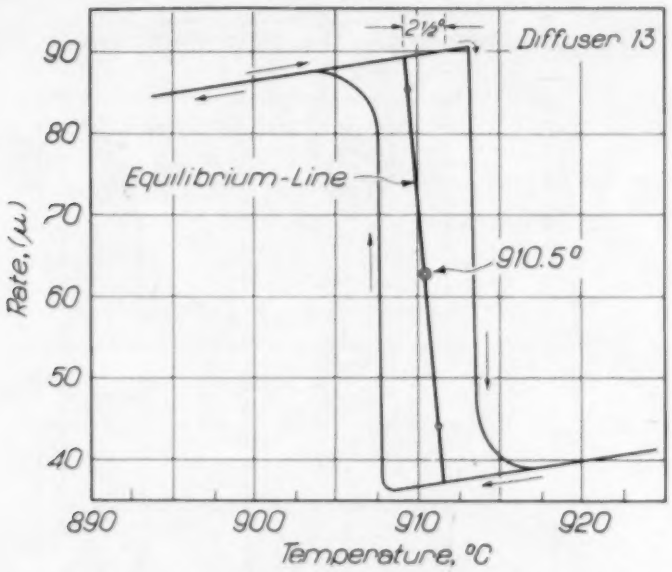


Fig. 3—Equilibrium Conditions at A_3. Impressed Pressure of Hydrogen 76 cm.

gen on the same diffuser, and observing the equilibrium condition of the body-centered–face-centered region as outlined above. The results of observations on the rate of diffusion through a sample of Mehl-iron when the pressure was varied from 73.4 to 17.5 cm. of mercury are shown graphically in Figs. 3, 4, and 5.

No great accuracy in obtaining the absolute temperature of transition was attempted. The thermocouple was calibrated when in place by means of the melting of a pure silver bead (see footnote 3).

Fig. 3 shows the variation of rate of diffusion with temperature when the entering pressure of hydrogen is 73.4 cm., the average exit pressure being 0.003 cm. The center of the equilibrium transition region appears at 910.5 degrees Cent. (1670 degrees Fahr.) on the chromel-alumel thermocouple.

Fig. 4 shows the same procedure as Fig. 3, but with the entering hydrogen pressure lowered to 19.5 cm., thereby making the mean

concentration of hydrogen about one-half as great. This is because the solubility of hydrogen in iron varies as the square root of the pressure in this temperature region. The center of the transition equilibrium region is now about 1 degree higher. We must emphasize the fact that the thermocouple was not accurately calibrated in this case. Hence the small deviation from the A_3 transition temperature obtained by Wells, Ackley and Mehl. This small deviation will not affect the conclusions reached as to the effect of concentration of hydrogen on the A_3 point.

Fig. 5 is for a different sample, assembled by a different technique. This will illustrate the precise study of allotropic transforma-

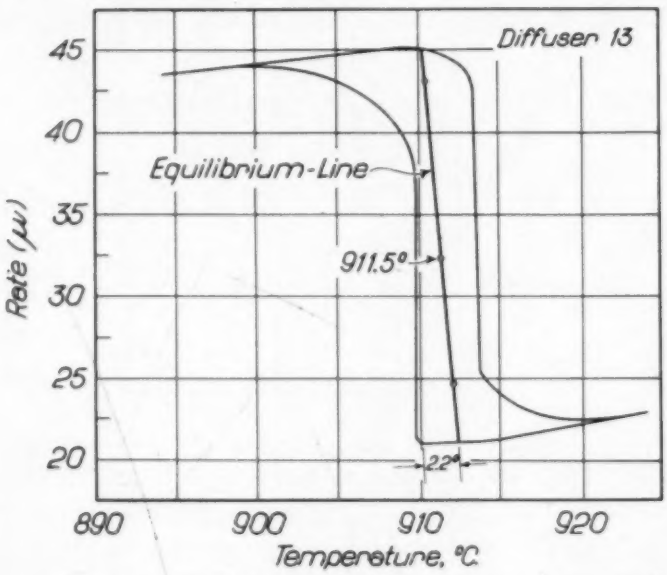


Fig. 4—Equilibrium Conditions at A_3. Impressed Pressure of Hydrogen 17.5 cm.

tion points made possible by our method. This sample was also carbonyl iron decarburized in Dr. Mehl's laboratory. It was pressed into a nickel tube, gold welded in a hydrogen atmosphere at the interface, machined to 0.060 inch thickness, then mounted in a diffusion apparatus in the usual way.

The temperature control was carefully adjusted and the body-centered–face-centered phases brought into equilibrium with rather low pressure (17 cm.) hydrogen on the entering side. The sample was then run through two different cycles of changes in the A_3 region. The pressure was then raised to atmospheric and a third cycle of changes taken in the same region. The effect is a lowering of the transition by almost exactly 1 degree, as might have been anticipated by a study of Figs. 3 and 4.

The best experimental value of the change is about 1 degree Cent., and means that if the sample were completely surrounded by hydrogen at these pressures a total variation of 2 degrees Cent. would be found. We are assuming the concentration of H_2 to be only one-half that found in solubility measurements because of the approximately zero-value of the concentration on the exit side. Thus, if the sample were completely surrounded by hydrogen as in the case of

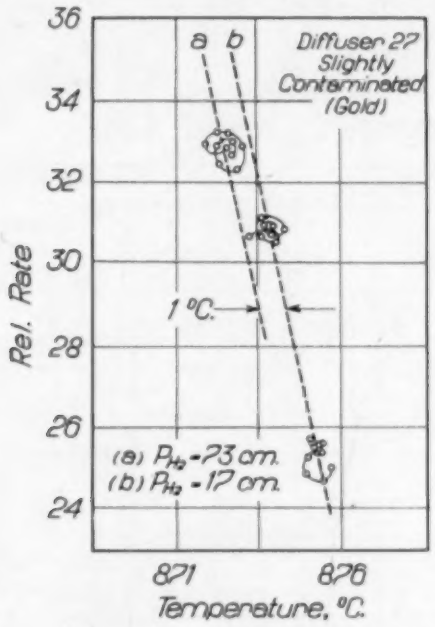


Fig. 5—Variation of Rate of Diffusion with Pressure of Hydrogen.

Roberts and Davey's[2] determination of the body-centered–face-centered point by X-ray methods, about 4 degrees should be added to the observed result. Incidentally, this will bring these investigators' results into agreement with those of Wells, Ackley and Mehl[1].

It appears from the data illustrated in Figs. 3, 4, and 5, that in such determinations as those made by Wells, Ackley and Mehl the residual hydrogen should have a negligible effect on the transition temperature given by these authors, particularly since isotherms taken between 74 and 1 cm. entering pressure follow the square root formula very exactly. Hence, when Wells, Ackley and Mehl changed to a neutral atmosphere, they automatically reduced the hydrogen concentration to less than one-eighth and this amount would lower the transition less than 0.5 degree Cent.

From thermodynamic considerations we would expect the effect of hydrogen in solution to be as follows: Let T_o be the true body-

centered–face-centered transition temperature for pure iron, and $\triangle H$ the increase in heat content in going from the face-centered to the body-centered form. Also, let k be the ratio of hydrogen solubility in the face-centered and body-centered forms, N_2 the mol-fraction of H^+ in solution in gamma-iron, at the temperature T, then it can be shown[5] that for these very dilute solutions of H_2 in Fe that

$$(1) \quad \frac{dT}{dN_2} = \frac{RT_0^2}{\triangle H}(k - 1)$$

If we take $\triangle H = -220$ cal/gm atom, $T_0 = 910$ degrees Cent., and $k = 0.69$ (see Sieverts[6] for any diffusion curve in this region) then $\frac{dT}{dN_2} = 0.878 \times 10^4$ deg/mol fraction H_2. Sieverts gives 0.8 mg H_2 per 100 g. as the solubility of H_2 in iron at the body-centered–face-centered transformation, or dN_2 (for H^+) $= 4.47 \times 10^{-4}$. Therefore $dT = 3.9$ degrees Cent. Consequently, we would expect hydrogen at one atmosphere pressure to lower the true temperature about 4 degrees Cent.

Conclusion

Hydrogen diffusion studies give a clear picture of the equilibrium region of an allotropic transformation such as A_3 in pure iron. The technique employed would also enable one to fix accurately the true temperature of A_3 if a suitable method is used for assembling a diffuser of pure Mehl iron without small contaminations.

The diffusion method has been used to furnish information about the effect of hydrogen solubility on the A_3 point, and it is shown that if previous measurements have been obtained in a hydrogen atmosphere at a pressure of one atmosphere, a correction of about 4 degrees Cent. must be added to the A_3 temperature. The result published by Wells, Ackley and Mehl[1] on the temperature of the body-centered–face-centered transition requires that less than 0.5 degrees Cent. be added to take account of possible hydrogen concentration.

We wish to express our thanks to Dr. R. F. Mehl for furnishing us with a supply of his highly decarburized carbonyl iron.

[5] Lewis and Randall, Thermodynamics, Chap. 20, McGraw-Hill, 1923.
[6] A. Sieverts, *Z. Physik. Chem.*, Vol. 77, 1911, p. 591.

THE EFFECTS OF SUBSTANTIAL ADDITIONS OF ALUMINUM, COBALT, TITANIUM AND COLUMBIUM ON THE PROPERTIES OF 80 NICKEL-20 CHROMIUM ALLOYS

By Arthur L. Sanford and Oscar E. Harder

Abstract

The effects of 2.5, 5, and 10 per cent additions of aluminum, cobalt, titanium and columbium on the properties of alloys of the 80 nickel-20 chromium type have been investigated. A commercial 80 nickel-20 chromium alloy was used as the base for comparison. Tensile and hot hardness tests up to 1000 degrees Cent. (1830 degrees Fahr.) were made. Resistance measurements at 20 degrees Cent. and life tests of 1175 and 1260 degrees Cent. (2145 and 2300 degrees Fahr.) were also made, as well as growth tests at 1040 degrees Cent. (1905 degrees Fahr.) and bend tests after heating to 1315 degrees Cent. (2400 degrees Fahr.).

The aluminum additions were the most beneficial, resulting in (1) increased tensile properties up to 800 degrees Cent. (1470 degrees Fahr.), except elongation at 600 to 800 degrees Cent. (1110 to 1470 degrees Fahr.), (2) increased hot hardness, (3) increased electrical resistance, and (4) increased life at 1175 and 1260 degrees Cent. A columbium addition of 10 per cent gave increased electrical resistance and increased tensile properties and hardness up to 1000 degrees Cent. The lower columbium and the titanium additions were less beneficial, resulting in slightly increased tensile properties at 600 to 1000 degrees Cent. (1110 to 1830 degrees Fahr.) and slightly increased electrical resistance. The cobalt additions were not beneficial to the properties studied. The experimental materials showed some growth in 100 hours at 1040 degrees Cent. (1905 degrees Fahr.), but retained their cold bending properties after heating to 1315 degrees Cent. (2400 degrees Fahr.).

Good correlation was found between the elevated temperature tensile tests and the mutual indentation hot hardness tests.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, Arthur L. Sanford is metallurgist and Oscar E. Harder is assistant director, Battelle Memorial Institute, Columbus, Ohio. Manuscript received July 25, 1938.

Introduction

THE commercial electric resistor alloys of today may be divided into two general classes: namely, (1) the alloys of nickel and chromium with or without substantial percentages of iron and (2) the alloys of the iron-chromium-aluminum group, some of which also contain small amounts of cobalt.

The principal alloys of the nickel-chromium group are the 80 nickel-20 chromium and 60 nickel-15 chromium-25 iron alloys. These alloys are austenitic in structure and possess good elevated temperature mechanical properties. They are also characterized by good resistance to growth, creep and distortion at their operating temperatures. The ohmic resistance of these alloys ranges from 650 to 675 ohms/c.m.f.

The iron-chromium-aluminum alloys possess higher ohmic resistances and better resistance to oxidation than the nickel-chromium and nickel-chromium-iron alloys. However, the elevated temperature mechanical properties of the ferritic iron-chromium-aluminum alloys are relatively poor. They are also subject to considerable growth at their operating temperatures. Manufacturing difficulties make the cost of the iron-chromium-aluminum alloys considerably higher than the cost of the nickel-chromium alloys.

The "ideal" resistor alloy should combine the electrical resistivity and oxidation resistance of the iron-chromium-aluminum alloys with the elevated temperature mechanical properties, resistance to growth and distortion, and the relative ease of manufacturing of the nickel-chromium and nickel-chromium-iron alloys.

This preliminary investigation has been confined to studying the effects of substantial additions of aluminum, cobalt, titanium, and columbium on the properties of alloys of the 80 nickel-20 chromium type. The effects of 2.5, 5, and 10 per cent additions of these elements on the room and elevated temperature tensile properties and hardness, on electrical resistivity, on the life of the alloys in the intermittent life test, on growth at 1040 degrees Cent. (1905 degrees Fahr.) and on cold bending properties after heating to 1315 degrees Cent. (2400 degrees Fahr.) have been studied. It is known that slight variations in the deoxidation or handling of alloys of this class may produce large changes in behavior, especially with respect to life tests, hence the results are chiefly of a compara-

tive nature since an attempt was made to handle all of the experimental heats alike.

Preparation of Alloys

The nominal compositions of the experimental alloys which were prepared and investigated are shown in Table I. Analysis of Alloy No. 1 and Alloy No. 2 showed 2.25 and 4.33 per cent aluminum, indicating about 90 per cent recovery.

Table I
Nominal Compositions of Experimental Alloys

Alloy No.	Composition—Per Cent									
	Ni	Cr	Al	Co	Ti	Cb	Si	Fe	Ta	Mn
1	78.0	19.5	2.5	(2.25% Al—by analysis)			...	...	...	...
2	76.2	19.0	4.8	(4.33% Al—by analysis)			...	...	...	...
3	72.7	18.2	9.1	...	...	...	...	...	...	..
4	78.0	19.5	...	2.5	...	...	...	...	...	...
5	76.2	19.0	...	4.8	...	...	...	...	...	...
6	72.7	18.2	...	9.1	...	...	...	...	...	...
7	78.0	19.5	...	...	2.5	...	...	...	...	...
8	76.2	19.0	...	...	4.8	...	...	...	...	...
9	72.7	18.2	...	...	9.1	...	...	...	...	...
10	76.5	19.1	...	...	...	2.5	0.35	1.2	0.20	0.15
11	73.4	18.4	...	...	...	4.7	0.65	2.3	0.35	0.30
12	67.9	17.0	...	...	...	8.6	1.20	4.2	0.65	0.50

The alloys were prepared in a 20-kilowatt high-frequency induction furnace using a magnesia crucible. Electrolytic nickel was melted and deoxidized with 0.05 per cent of calcium-silicide. Commercial 98 per cent chromium was added and melted to form the base alloy of 80 nickel-20 chromium. After deoxidation with 0.10 per cent of metallic calcium, the aluminum, cobalt, titanium, or columbium was added. Commercial aluminum, 98 per cent cobalt, 98 per cent titanium and ferrocolumbium were used to make the additions. The alloys were cast as 5-pound ingots. The pouring temperature varied from 1480 to 1540 degrees Cent. (2700 to 2800 degrees Fahr.).

The ingots were forged to 1¼-inch square bars and hot-rolled to ¼-inch round rods. The forging and hot rolling temperature was about 1150 degrees Cent. (2100 degrees Fahr.). Although the alloys were very stiff at the hot working temperature, most of them were readily forged and rolled, but required numerous reheatings. The 10 per cent aluminum and titanium alloys cracked badly during forging and were discarded.

The ¼-inch rods were hot-swaged at about 1150 degrees Cent. (2100 degrees Fahr.) to wire 0.107-inch in diameter. The hot-swaged wire was annealed for one-half hour at 1040 degrees Cent. (1900 degrees Fahr.), sand blasted to remove the scale, and cold drawn to 0.102-inch diameter. Most of the cobalt alloys were given a further reduction to 0.091 inch.

Testing Methods and Equipment

Tensile Tests: The tensile tests were made using a mechanically driven testing machine of 1000-pound capacity. The head speed of the testing machine was 0.10 inch per minute. The tensile specimens were 12 inches long and marked with ¼-inch (± 0.005-inch) gage marks over the center 6 inches. The per cent elongation in 6 inches was derived from the extension occurring in the marked 6 inches regardless of the position of the fracture, although this was generally within the center 2 inches. In calculating the per cent elongation in ½ inch (roughly five times the diameter) an "inverse lever arm" method was used to adjust the position of the fracture to the center of the ½ inch used. The yield strength values were taken at the points where the stress-strain curves deviated perceptibly from a straight line.

For the elevated temperature tensile tests a small electric furnace, 6¼ inches long, was constructed with provisions made for shunting the center 3 inches of the winding so that a uniform temperature zone of at least 2 inches could be maintained. The results of the furnace calibration at 200, 400, 600, 800, and 1000 degrees Cent. are shown in Fig. 1. The temperature variation in the center 2 inches was 4 degrees Cent. or less up to 800 degrees Cent. and was 6 degrees Cent. at 1000 degrees Cent. Tensile specimens were held 10 minutes at temperature before loading.

Hardness Tests: The elevated temperature hardness tests were made by the mutual indentation method which has been fully described by Harder and Grove (1)[1] and need not be discussed here. The specimens for the hot hardness tests were machined from ½-inch square stock cut from bars after hot rolling. The mutual indentation hardness tests were supplemented by room temperature Rockwell "B" and "D" tests made before and after the elevated temperature tests.

Electrical Resistance Measurements: The room temperature

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

electrical resistance measurements were made on a Kelvin double bridge using specimens 35 centimeters long. The hot resistance data were obtained from the life tests.

Life Tests: The life testing equipment and procedure were similar to those described by Hoyt and Scheil (2) and need not be discussed in detail. While Hoyt and Scheil found it desirable to test their iron-chromium-aluminum alloy under no load conditions, the A.S.T.M. standard stress of 35 pounds per square inch was

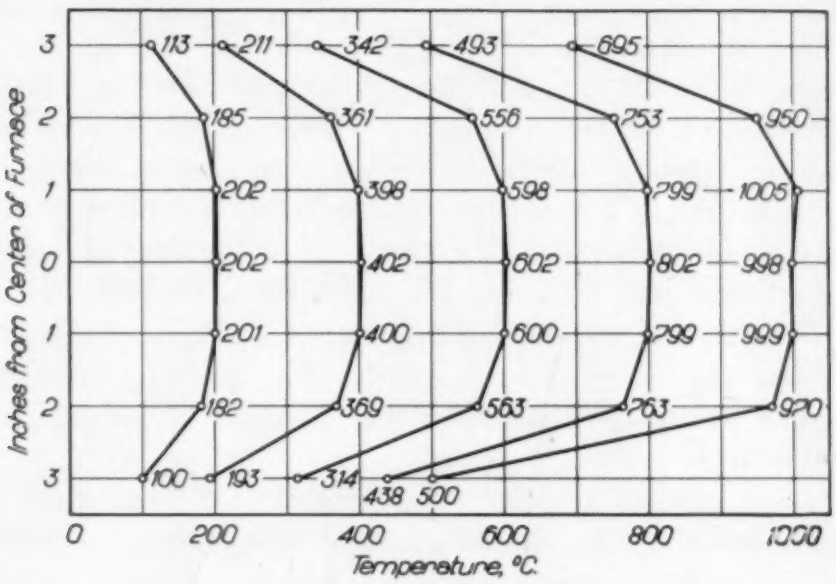


Fig. 1—Calibration Results on Elevated Temperature Tensile Furnace.

applied to the wires in these tests. An intermittent cycle of 2 minutes on and 3 minutes off was used. In conformation with general practice in life testing of resistor materials, the useful life was taken as the life to a 10 per cent increase in hot electrical resistance.

Growth and Bend Tests: Relatively long time growth tests were made by heating specimens continuously for 100 hours at 1040 degrees Cent. (1905 degrees Fahr.). Some short time growth tests were made by heating additional specimens 6 hours at 1090 degrees Cent. (1995 degrees Fahr.) plus 2 hours at 1315 degrees Cent. (2400 degrees Fahr.). Length measurements were made before and after heating. Repeated 180-degree bend tests (radius of bend about ⅛ inch) were made on the growth test specimens after heating to 1315 degrees Cent. (2400 degrees Fahr.).

Tensile Tests

Tensile tests were made at room temperature and at 400, 600, 800, and 1000 degrees Cent. (750, 1110, 1470, 1830 degrees Fahr.) on the experimental alloys which had been successfully reduced to cold drawn wire. Tests were made on commercial 80 nickel-20 chromium resistor wire (0.081 inch) at the same temperatures as the bases for comparison. Duplicate tests were made on each alloy at each temperature, except 400 degrees Cent. (750 degrees Fahr.). All tensile specimens were annealed ½ hour at 1000 degrees Cent. (1830 degrees Fahr.) before testing.

The results of the tensile tests are given in Table II and in Figs. 2 to 6, inclusive. Where single curves are shown for more than one alloy, the averages of the values in Table II for these alloys have been plotted.

Room Temperature Properties: The room temperature tensile strengths covered a range from 95,000 to 153,000 pounds per square inch, with the commercial 80 nickel-20 chromium alloy about midway in this range. Three of the experimental alloys (2.5 and 5 per cent aluminum and 10 per cent columbium) had tensile strengths from 18,000-32,000 pounds per square inch higher than the commercial 80 nickel-20 chromium alloy. The tensile strengths of the remaining experimental alloys fell in two groups, (1) 95,000-100,000 pounds per square inch for the cobalt alloys and (2) 111,000-115,000 pounds per square inch for the titanium and low columbium (2.5 and 5.0 per cent) alloys.

The aluminum and 10 per cent columbium alloys also had higher yield strengths and lower elongation than the commercial 80 nickel-20 chromium alloy. The elongation of these alloys was fairly good. however, (25 per cent in 0.5 inch). The yield ratios of these alloys were 0.63 for the aluminum alloys and 0.54 for the 10 per cent columbium alloy compared with 0.50 for the commercial alloy.

The cobalt, titanium, and low columbium (2.5 and 5 per cent) alloys, which showed decreased tensile strengths, also showed decreased yield strengths, decreased yield ratios, and in some cases an increase in elongation in comparison with the commercial 80 nickel-20 chromium alloy. The yield ratios of these alloys varied from 0.40 to 0.45.

Elevated Temperature Properties: The mechanical properties of the commercial 80 nickel-20 chromium alloy (Fig. 6) change but

Table 11

Results of Tensile Tests at 20, 400, 600, 800, and 1000 Degrees Cent. on Annealed Electric Resistor Alloys. Each Value is the Average of Two Tests Except for Single Tests at 400 Degrees Cent.

Test Temperature			20° C.				400° C.				600° C.			
Alloy No.	Alloy	Diam. In.	Yield Strength p.s.i.	Tensile Strength p.s.i.	Elongation, % 0.5 In.	Elongation, % 6 In.	Yield Strength p.s.i.	Tensile Strength p.s.i.	Elongation, % 0.5 In.	Elongation, % 6 In.	Yield Strength p.s.i.	Tensile Strength p.s.i.	Elongation, % 0.5 In.	Elongation, % 6 In.
1	2.5 Al	0.102	92,000	144,000	25.0	18.0	91,000	(a)	...	...	87,250	92,750	3.5	1.0
2	5.0 Al	0.102	94,600	153,000	25.0	19.5	93,000	(a)	...	...	87,250	92,750	3.5	1.0
4	2.5 Co	0.091	37,000	95,600	53.0	35.0	32,300	88,000	(b)	30.0	24,000	65,500	24.0	17.5
5	5.0 Co	0.091	40,000	98,750	42.0	31.0	37,000	95,800	40.5	26.0	27,500	61,500	17.0	11.5
6	10.0 Co	0.091	41,400	100,000	41.5	32.0	35,400	94,100	40.5	26.0	25,800	64,400	20.0	13.0
7	2.5 Ti	0.102	50,000	113,000	48.0	42.5	46,500	104,750	48.0	31.5	35,700	81,500	34.0	23.0
8	5.0 Ti	0.102	44,500	111,000	59.0	40.5	34,900	106,250	(b)	39.0	32,700	81,000	30.5	21.5
10	2.5 Cb	0.102	51,250	112,000	44.0	31.0	39,800	107,500	39.5	28.0	44,000	80,500	27.0	14.0
11	5.0 Cb	0.102	51,250	115,000	50.0	36.0	42,800	110,400	47.5	21.0	35,700	80,750	25.0	17.0
12	10.0 Cb	0.102	75,100	139,000	25.0	24.0	69,000	(a)	...	...	58,250	105,000	23.5	15.0
Commercial 80 Ni-20 Cr		0.081	59,000	121,000	44.5	32.0	48,000	113,000	40.0	26.0	38,800	77,700	26.0	14.0

Test Temperature			800° C.				1000° C.			
1	2.5 Al	0.102	(d)	50,750	2.5	0.5	5,100	7,700	30.0	11.0
2	5.0 Al	0.102	(d)	48,300	3.0	1.0	4,900	8,200	30.0	11.0
4	2.5 Co	0.091	19,500	23,100	34.0	14.0	5,800	8,600	19.5	6.0
5	5.0 Co	0.091	19,000	21,700	25.5	11.0	6,200	8,600	19.5	7.0
6	10.0 Co	0.091	18,100	21,000	26.5	11.0	6,500	8,900	36.0	12.0
7	2.5 Ti	0.102	30,900	32,850	45.5	25.0	6,400	9,600	34.0	14.0
8	5.0 Ti	0.102	25,700	28,900	55.5	24.0	6,400	9,600	46.5	15.0
10	2.5 Cb	0.102	29,400	33,000	42.0	13.5	7,200	10,700	38.0	13.0
11	5.0 Cb	0.102	27,500	30,200	52.0	17.0	6,900	10,100	22.5	8.0
12	10.0 Cb	0.102	35,500	38,500	60.0	16.0	6,100	9,700	53.0	16.5
Commercial 80 Ni-20 Cr		0.081	18,400	25,100	35.0	14.0	5,100	8,100	30.0	11.0

(a) Tensile strength over 122,000 p.s.i specimen too strong for 1000 lb. testing machine.

(b) Broke outside of uniform temperature zone in furnace.

(c) Flawed specimens. Results are for single tests.

(d) No definite yield point.

little as the temperature is increased to 400 degrees Cent. Above 400 degrees Cent. the yield strength and tensile strength drop off rapidly, the rate of decrease increasing with the temperature up to 800 degrees Cent. and decreasing somewhat at 1000 degrees Cent. (1830 degrees Fahr.). The ductility as indicated by the elongation in ½-inch drops to a minimum at 600 degrees Cent. (1110 degrees Fahr.), rises at 800 degrees Cent. (1470 degrees Fahr.), and falls again at 1000 degrees Cent. (1830 degrees Fahr.). The elongation in 6 inches showed no minimum at 600 degrees Cent. (1110 degrees Fahr.), but did level off from 600 to 1000 degrees Cent. (1110 to 1830 degrees Fahr.).

Quier (3) and Pilling and Worthington (4) have given data on the mechanical properties of alloys of the 80 nickel-20 chromium type. The results for the present 80 nickel-20 chromium alloy are in excellent agreement with the values found by Quier. The variation in tensile strength from Quier's data is not over 5000 pounds per square inch up to 600 degrees Cent. (1110 degrees Fahr.), and is only 1000 pounds per square inch at 800 and 1000 degrees Cent. (1470 and 1830 degrees Fahr.). Quier's ductility curves for elongation and reduction of area showed minimums at 595 degrees Cent. (1100 degrees Fahr.), rose to maximums at about 705-735 degrees Cent. (1300-1350 degrees Fahr.) and fell again at higher temperatures. This corresponds well with the present minimum at 600 degrees Cent. (1110 degrees Fahr.), the rise at 800 degrees Cent. (1470 degrees Fahr.) and the drop at 1000 degrees Cent. (1830 degrees Fahr.).

At 400 degrees Cent. the tensile strength curves for the aluminum alloys (Fig. 2) and the 10 per cent columbium alloy (Fig. 5) have been drawn through 140,000 and 132,000 pounds per square inch respectively, since the specimens were too strong for the capacity of the testing machine used for the elevated temperature tensile tests. These values of 140,000 and 132,000 pounds per square inch were determined by averaging the slopes of the tensile curves for the other alloys from 20 to 400 degrees Cent. The same applies to the tensile strength of the aluminum alloys at 600 degrees Cent. (112,000 pounds per square inch in Fig. 2), since the specimens broke in flawed areas and no additional material was available.

The changes in the mechanical properties of the experimental alloys at elevated temperatures correspond well with the changes for the commercial 80 nickel-20 chromium alloy. The tensile and

yield strengths decrease but slightly at 400 degrees Cent., fall with increasing rates from 400 to 800 degrees Cent., and at somewhat slower rates from 800 to 1000 degrees Cent. (1470 to 1830 degrees Fahr.). At 800 degrees Cent. (1470 degrees Fahr.) the tensile strengths were generally about 25 to 30 per cent of the room temperature values.

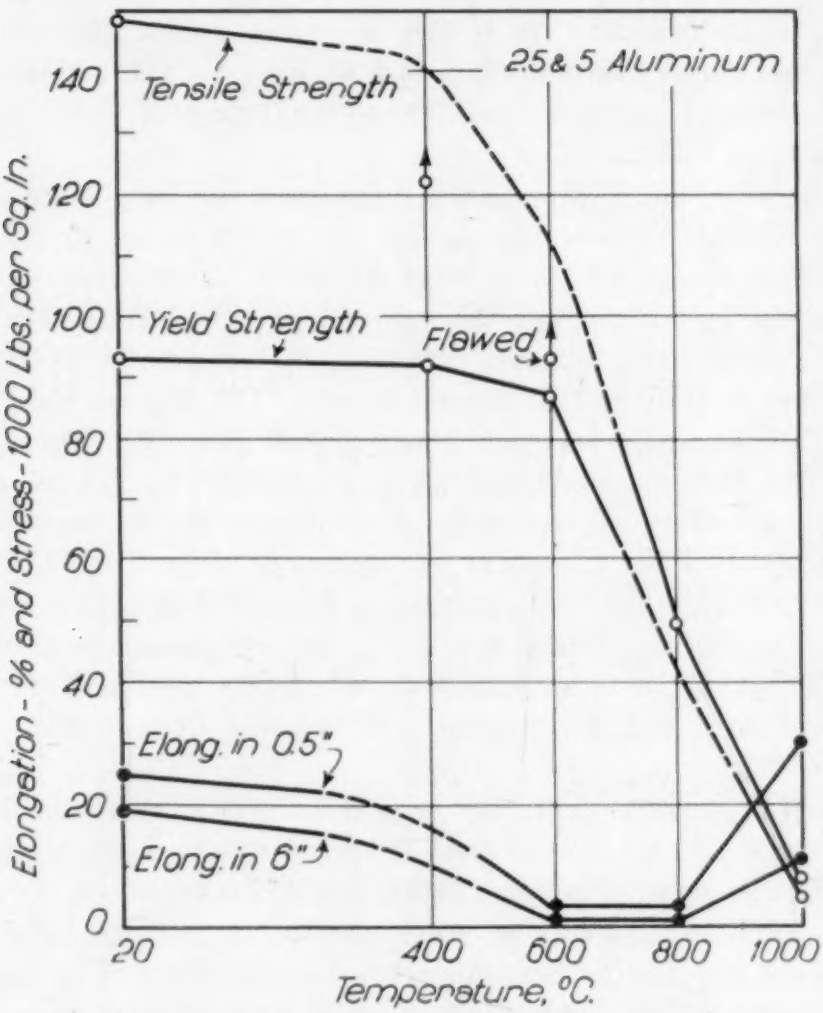


Fig. 2—Aluminum Alloys. Results of Room and Elevated Temperature Tensile Tests on Annealed Electric Resistor Alloys.

The changes in the ductility (elongation in 0.5 inch) with temperature for the cobalt, titanium, and columbium alloys followed the same trends as the 80 nickel-20 chromium alloy with minimums at 600 degrees Cent. (1110 degrees Fahr.), sharp recoveries to maximums at 800 degrees Cent. (1470 degrees Fahr.), and another drop at 1000 degrees Cent. (1830 degrees Fahr.). The minimum elonga-

tion values at 600 degrees Cent. (1110 degrees Fahr.) do not indicate poor ductility, however, since none of these alloys had less than 20 per cent elongation in 0.5 inch at this temperature. On the other hand, the ductility of the aluminum alloys was poor in the region from 600 to 800 degrees Cent. (1110 to 1470 degrees Fahr.), but recovered sharply at 1000 degrees Cent. (1830 degrees Fahr.).

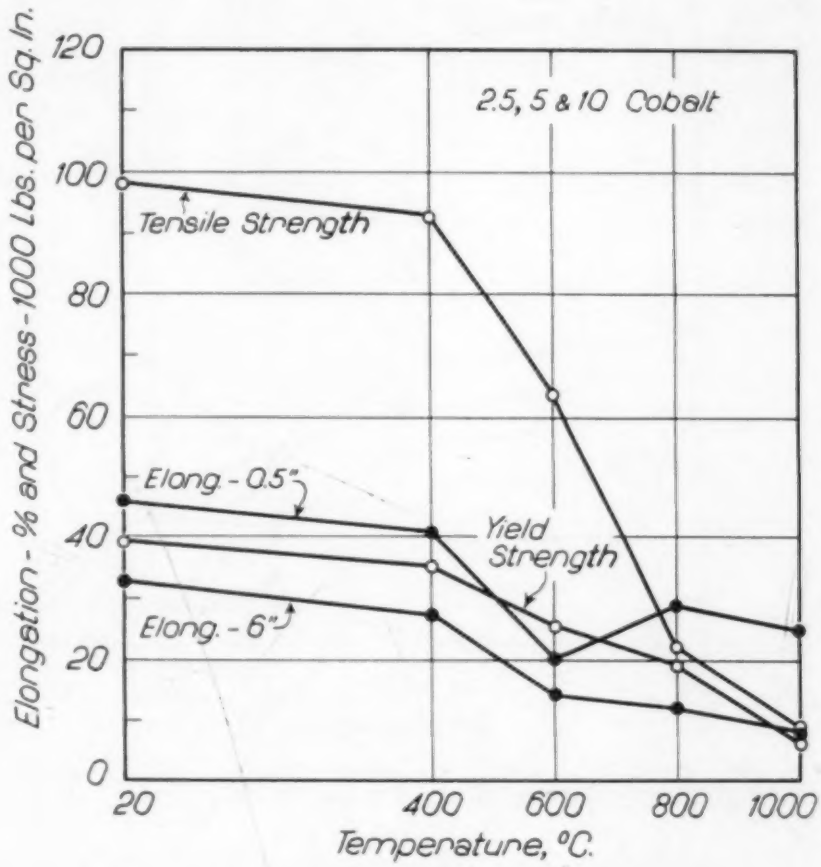


Fig. 3—Cobalt Alloys. Results of Room and Elevated Temperature Tensile Tests on Annealed Electric Resistor Alloys.

The superiority of the aluminum and 10 per cent columbium alloys over the commercial 80 nickel-20 chromium alloy (see Fig. 7) in respect to tensile strength is maintained up to 800 degrees Cent. (1470 degrees Fahr.). The titanium and low columbium (2.5 and 5 per cent) alloys, which had slightly lower tensile strengths than the 80 nickel-20 chromium alloy at 20 and 400 degrees Cent., have small advantages over the 80 nickel-20 chromium alloy at 600 and 800 degrees Cent. At 1000 degrees Cent. the columbium and titanium alloys had the highest tensile strengths, while the aluminum

alloys together with the commercial 80 nickel-20 chromium alloy had the lowest strengths.

The relatively poor elevated temperature tensile strength of one of the iron-chromium-aluminum-cobalt resistor alloys is shown

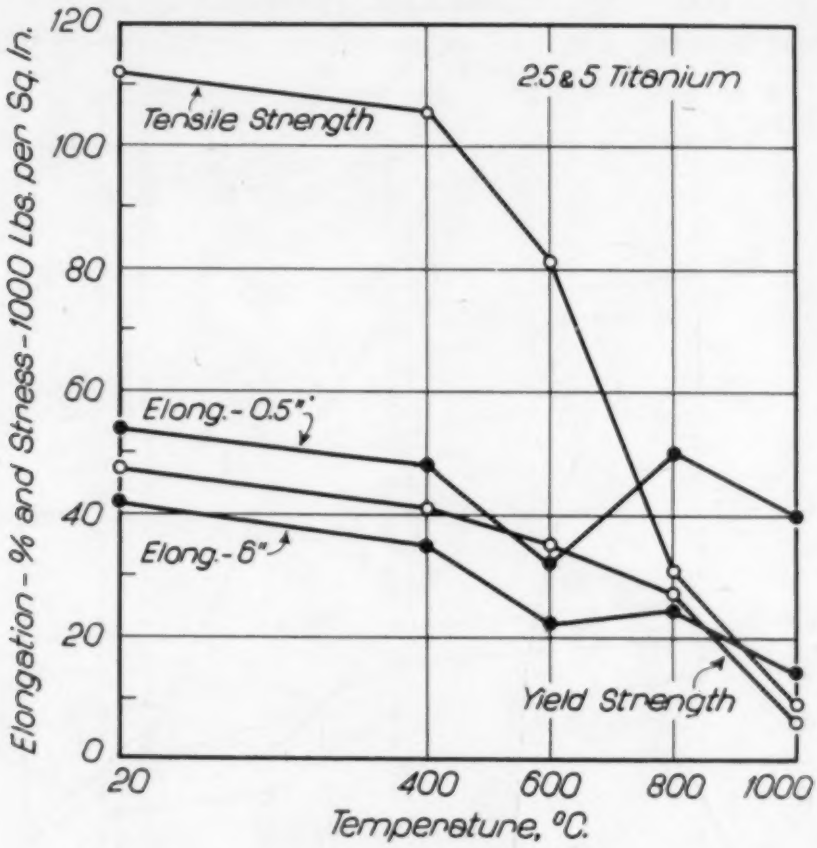


Fig. 4—Titanium Alloys. Results of Room and Elevated Temperature Tensile Tests on Annealed Electric Resistor Alloys.

in Fig. 7 for comparison with the commercial 80 nickel-20 chromium alloy and the present experimental alloys. The data for the iron-chromium-aluminum-cobalt alloy were taken from Nordström (5, 6). At 1000 degrees Cent. the tensile strength of this alloy is 2800 pounds per square inch compared with 8000-8600 pounds per square inch for the 80 nickel-20 chromium and the experimental aluminum and cobalt alloys and with 9600 to 10,700 pounds per square inch for the experimental titanium and columbium alloys.

Hot Hardness Tests

Mutual indentation hot hardness tests were made on the experimental alloys at 400, 600, 700, 800, and 1000 degrees Cent. (750,

1110, 1290, 1470, and 1830 degrees Fahr.). No hot hardness tests were made on the commercial 80 nickel-20 chromium alloy. The results of the hot hardness tests are given in Table III and in Fig. 8. Table IV gives the results of the supplementary Rockwell "B" or "D" tests made at room temperature before and after the hot hard-

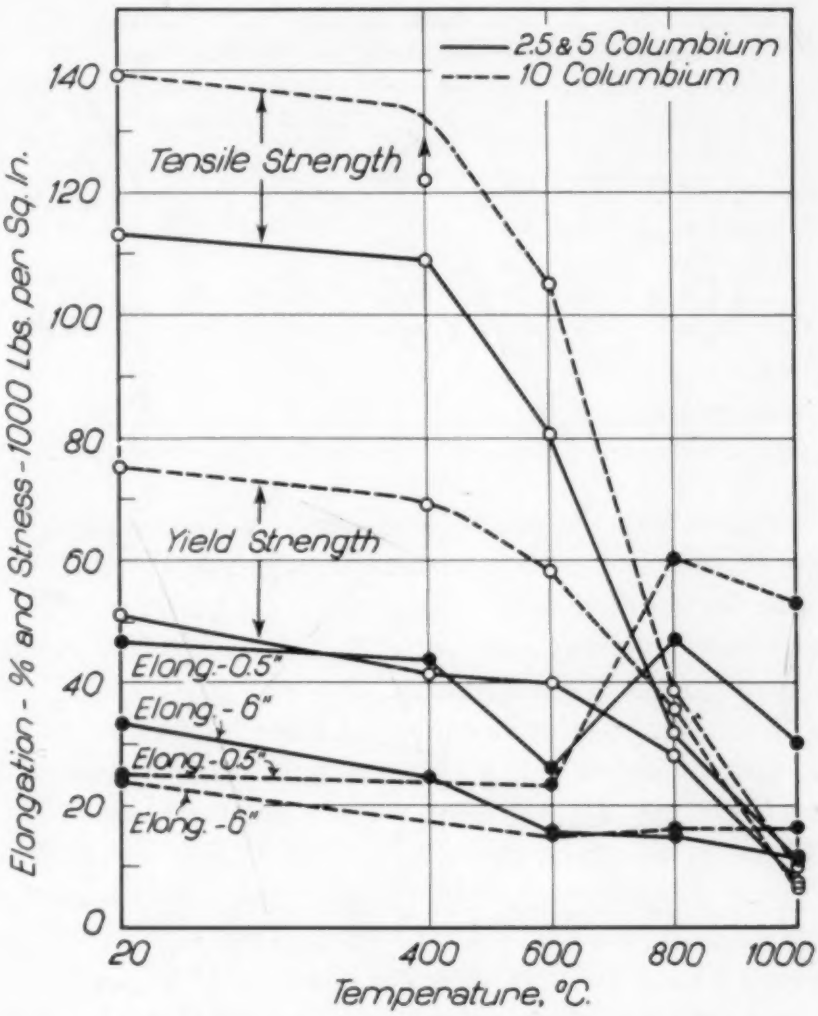


Fig. 5—Columbium Alloys. Results of Room and Elevated Temperature Tensile Tests on Annealed Electric Resistor Alloys.

ness tests. As was the case with the elevated temperature tensile data, single curves have been plotted in Fig. 8 for the hot hardness of similar alloys in some instances; for example, the 2.5 and 5 per cent aluminum alloys.

The similarity between the hot hardness curves and the tensile strength curves is very striking. The positions of the various alloys in Figs. 7 and 8 are the same with the exception of the hot hardness

curve for the 5 per cent titanium alloy. The hot hardness values for this alloy would probably have been lower and close to those of the 2.5 per cent titanium alloy had the hot hardness specimens been annealed at 1000 degrees Cent. (1830 degrees Fahr.) before testing,

Table III
Results of Mutual-Indentation Hot Hardness Tests

Alloy No.	Alloy	Brinell Hardness at 20° C.*	400° C.	600° C.	700° C.	800° C.	1000° C.
1	2.5 Al	280	238	218	190	105	21
2	5.0 Al	290	248	234	203	122	23
4	2.5 Co	155	123	94	73	50	25
5	5.0 Co	155	109	76	80	58	27
6	10.0 Co	155	111	76	71	54	25
7	2.5 Ti	200	152	132	112	68	26
8	5.0 Ti	270	226	217	210	89	26
10	2.5 Cb	170	128	122	95	61	27
11	5.0 Cb	170	117	108	92	61	30
12	10.0 Cb	225	179	159	145	92	32

*Conversion from Rockwell "B" or "D".

as was the case with the tensile specimens. This is indicated by the proximity of the elevated temperature tensile data for these titanium alloys, and the marked drop in the room temperature hardness of the 5 per cent titanium alloy after hot hardness testing at 1000 degrees Cent. (1830 degrees Fahr.).

The room temperature hardness of these alloys covered a range from 155 Brinell for the cobalt alloys to 285 Brinell for the aluminum alloys. At 400 and 600 degrees Cent. the hot hardness of all of the alloys decreased at fairly uniform rates. At 700 and 800 degrees Cent. the rate of hardness loss increased rapidly, the increase in rate being the greatest for those alloys having the highest hardness at 600 degrees Cent. At 1000 degrees Cent. (1830 degrees Fahr.) the alloys which had the highest hardness at lower temperatures have lost their advantage almost entirely, as the Brinell hardness at 1000 degrees Cent. (1830 degrees Fahr.) varied only from 21 to 32. However, the relation between the hot hardness and the tensile strength data at 1000 degrees Cent. (1830 degrees Fahr.) is still good with the aluminum alloys the lowest in each case, while the columbium alloys were highest, with the titanium and cobalt alloys in between. The supplementary hardness tests (Table IV) showed no marked drop in room temperature hardness after hot hardness testing except for 5 per cent titanium alloy as already noted.

Electrical Resistance

Room temperature electrical resistance measurements were made on specimens which had been annealed 0.5 hour at 1000 degrees Cent. (1830 degrees Fahr.). The hot resistance data were obtained from measurements made during the first hour of the life tests. The results of the electrical resistivity measurements are shown in Table V.

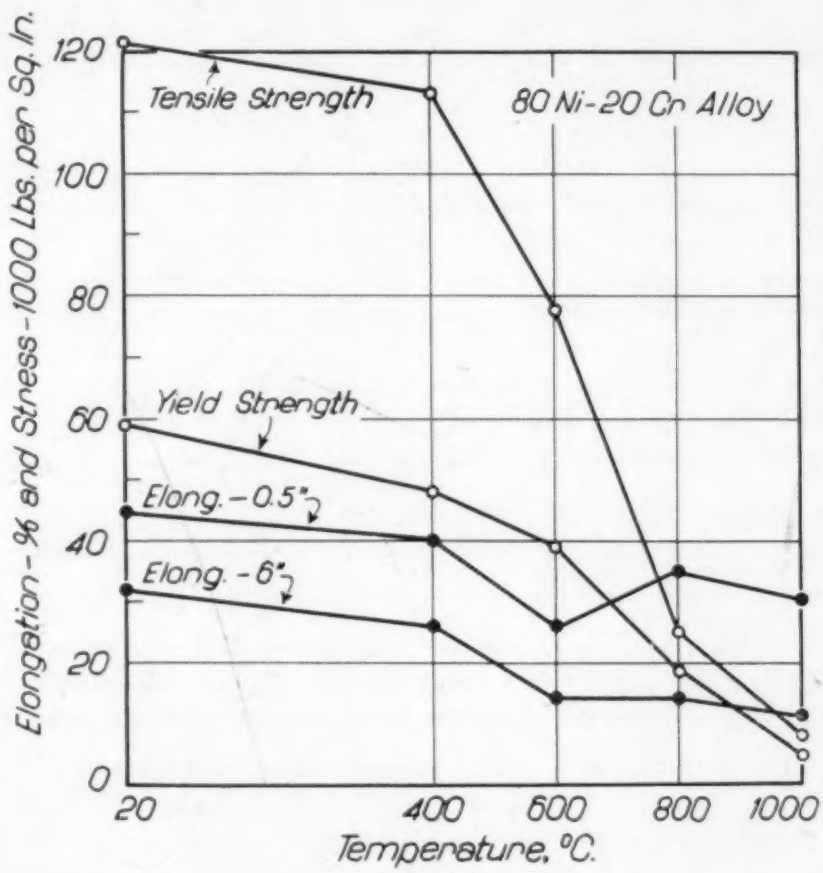


Fig. 6—Results of Room and Elevated Temperature Tensile Tests on Commercial 80 Nickel-20 Chromium Electric Resistor Alloys.

The additions of aluminum, titanium, and columbium were beneficial in that the resistance at 20 degrees Cent. was higher than for the commercial 80 nickel-20 chromium. The aluminum alloys had the highest resistance of the experimental materials, 26 per cent higher than the 80 nickel-20 chromium, which puts this material in the resistance range covered by some of the iron-chromium-aluminum-cobalt alloys.

The aluminum alloys had the least increase in resistance at 1175 degrees Cent. (2150 degrees Fahr.), but showed considerable increase at 1260 degrees Cent. (2300 degrees Fahr.).

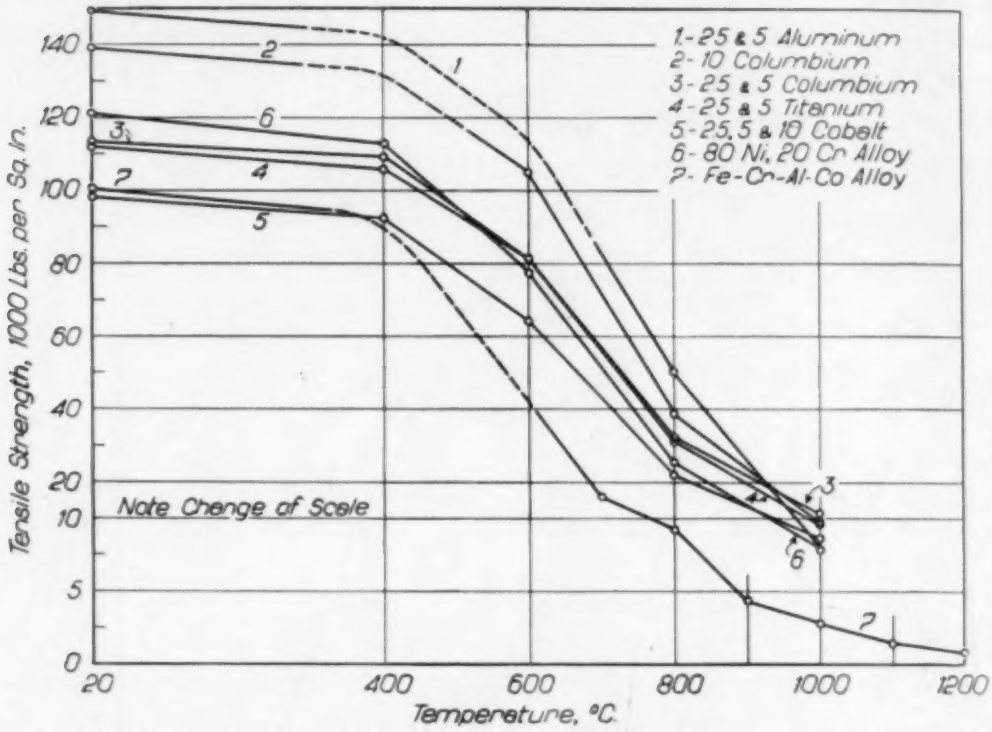


Fig. 7—Comparison of Elevated Temperature Tensile Strengths of Experimental Resistor Alloys with Commercial 80 Nickel-20 Chromium and with Iron-Chromium-Aluminum-Cobalt Alloys.

Table IV
Results of Room Temperature Hardness Tests Made After Hot Hardness Tests*

No.	Alloy	Brinell Hardness after Testing at 20° C.	400° C.	600° C.	700° C.	800° C.	1000° C.
1	2.5 Al	280	290	290	290	270	250
2	5.0 Al	290	280	290	290	270	255
4	2.5 Co	155	160	160	150	150	145
5	5.0 Co	155	155	155	155	150	145
6	10.0 Co	155	165	160	160	160	145
7	2.5 Ti	200	195	195	200	195	160
8	5.0 Ti	270	270	280	280	215	175
10	2.5 Cb	170	180	180	165	170	165
11	5.0 Cb	170	180	180	165	170	165
12	10.0 Cb	225	215	220	220	225	220

*All values by conversion from Rockwell "B" or "D".

Life Tests

Life tests were made on the 2.5 per cent cobalt, 5 per cent titanium, 2.5 and 5 per cent columbium, and the 2.5 and 5 per cent aluminum alloys, as well as the commercial 80 nickel-20 chromium

alloy. Two test temperatures were used, namely, 1175 and 1260 degrees Cent. (2150 and 2300 degrees Fahr.). The results of the life tests are given in Table VI, while Fig. 9 shows typical increase in resistance versus time curves.

At 1175 degrees Cent. (2150 degrees Fahr.) the 2.5 per cent alu-

Table V

Electrical Resistance Measurements on Annealed Resistor Alloys

Alloy No.	Alloy	Electrical Resistance at 20° C. Ohms/c.m.f.	Per Cent of 80 Ni-20 Cr	Electrical Resistance at 1175° C. Ohms/c.m.f.	Per Cent of Cold Resistance
1	2.5 Al	820	126	873	106
				1028 (1260° C.)	125
2	5.0 Al	820	126	1056 (1260° C.)	129
4	2.5 Co	625	96	748	120
				878 (1260° C.)	140
5	5.0 Co	611	94	...	...
6	10.0 Co	611	94	...	...
7	2.5 Ti	733	112	...	...
8	5.0 Ti	706	108	792	112
10	2.5 Cb	693	106	781	113
11	5.0 Cb	682	105	775	114
12	10.0 Cb	766	118	...	...
Commercial	80 Ni-20 Cr	652	100	710 (1260° C.)	109

minum and cobalt alloys showed lives of about 70 hours to a 10 per cent increase in resistance. The remaining alloys threw their scale and burned out in 16 to 18 hours. At 1260 degrees Cent. (2300 degrees Fahr.) the advantage of the aluminum alloys became apparent when the 2.5 per cent alloy had a useful life of 35 hours and the 5 per cent alloy 53 hours, while the 80 nickel-20 chromium alloy had a life of 22 hours.

It has been suggested by Hoyt and Scheil (2) that the relation between the life of a resistor and the temperature is an exponential one. Pertinent data were secured from the literature (2, 5-12) and plotted in this manner in Fig. 10 and results for the 2.5 and 5 per cent aluminum alloys have been included. The data for the 37.5 chromium-7.5 aluminum alloy and the 2.5 and 5 per cent aluminum alloys were reduced from 7.5 and 5-minute cycles, respectively, to 4-minute cycles (which is the A.S.T.M. Standard) since it has been

shown by Hessenbruch and Rohn (6) and by Bash and Harsch (13) that the life of resistors is approximately proportional to the length of cycle used in the testing.

That the exponential relationship holds is evident, though the

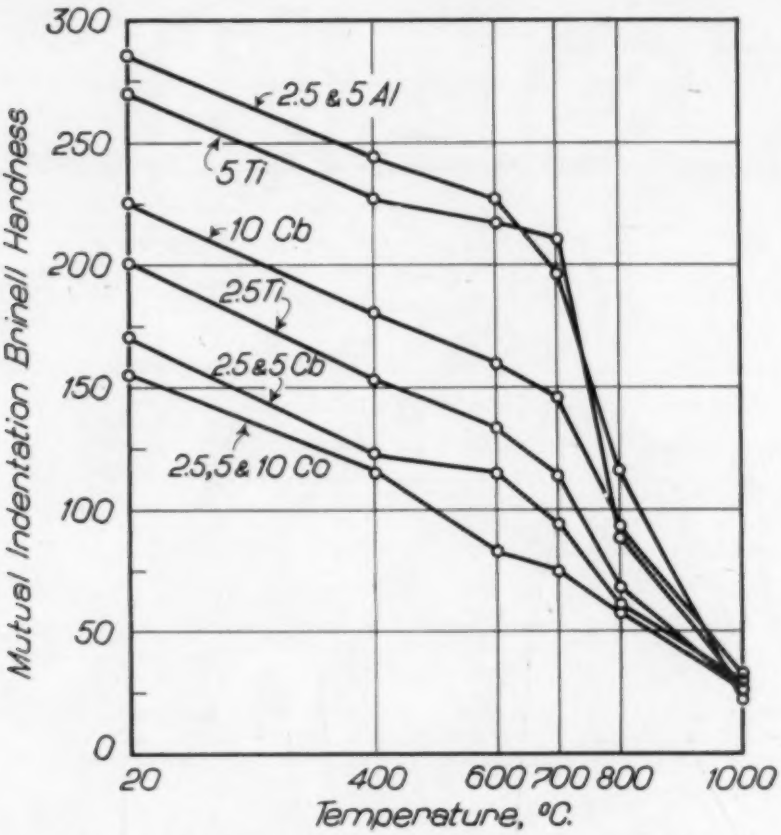


Fig. 8—Results of Mutual Indentation Hot Hardness Tests on Experimental Electric Resistor Alloys.

slope of the lines may vary slightly for different classes of alloys. The 2.5 per cent aluminum alloy occupies a position between the 80 nickel-20 chromium and the 25 chromium-4.5 aluminum-2.5 cobalt alloys, while the 5 per cent aluminum alloy lies between the 25 chromium-5 aluminum-3 cobalt and the 25 chromium-4.5 aluminum-2.5 cobalt alloys.

Growth and Bend Tests

The growth tests which have been made on the experimental alloys and on certain commercial alloys are inadequate for a complete appraisal of the stability or relative stability of these alloys. While it is realized that repeated heating and cooling tests over

long periods of time are necessary for a final evaluation of electric resistor alloys and such tests have not been made, some data on

Tabe VI
Results of Life Tests

Alloy	Temp. ° C.	Hours Life to 10% Increase in Hot Resistance	Remarks
2.5 Al	1175	69	Removed after 72 Hours
2.5 Co	1175	70	Removed after 72 Hours
5.0 Ti	1175	..	Burn Out—18 Hours
2.5 Cb	1175	..	Burn Out—18 Hours
5.0 Cb	1175	..	Burn Out—16 Hours
2.5 Al	1260	35	Removed at 54 Hours (Resistance up 17%)
5.0 Al	1260	53	Removed after 60 Hours (Resistance up 14%)
2.5 Co	1260	..	Burn Out—18 Hours
80 Ni-20 Cr	1260	22	Burn Out—52 Hours

growth have been obtained and are shown in Table VII. Specimens of the experimental alloys and of the commercial alloys were heated at 1040 degrees Cent. (1900 degrees Fahr.) for 100 hours and the increase in length was then determined. This temperature may be considered a normal operating temperature for 80 nickel-20 chro-

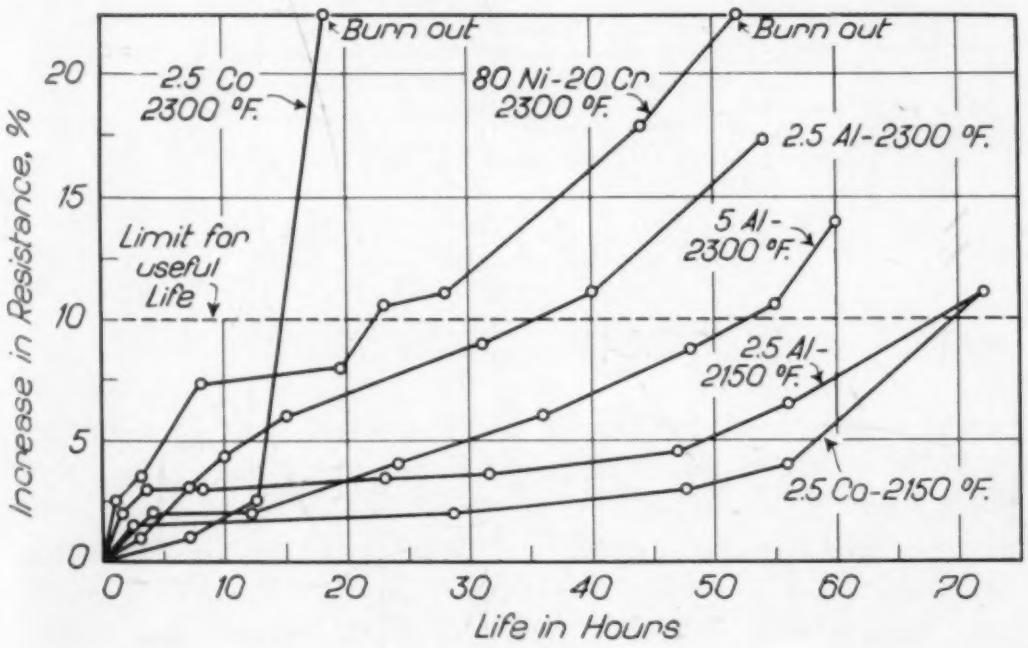


Fig. 9—Results of Life Tests.

mium but is considerably below the maximum operating temperature for iron-chromium-aluminum or iron-chromium-aluminum-cobalt alloys. In these tests the experimental alloys showed growths (except for 2.5 per cent titanium) of 0.001 to 0.009 inch per foot and compared unfavorably with 80 nickel-20 chromium and with the iron-chromium-aluminum-cobalt type alloys. The iron-chromium-aluminum alloy, however, in this relatively mild test

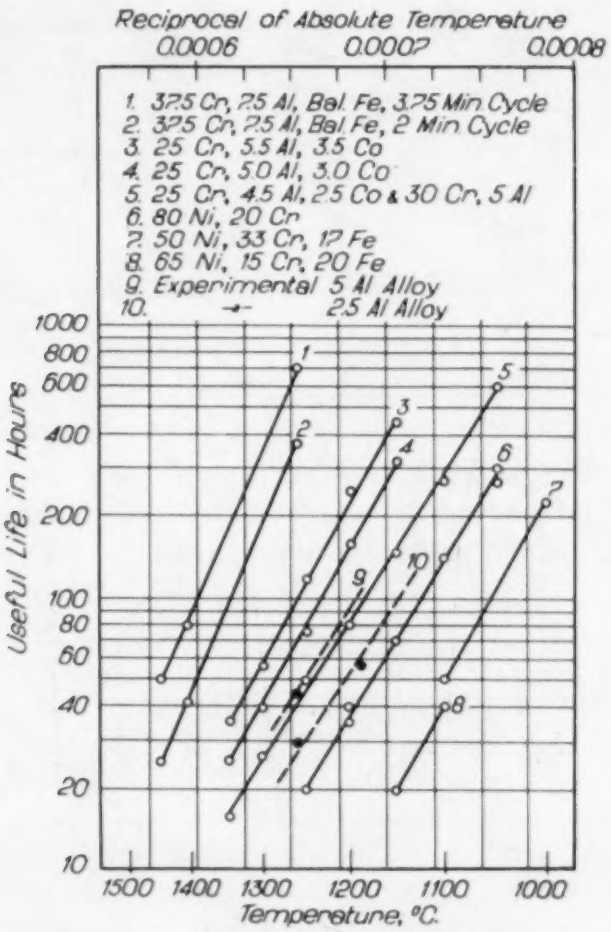


Fig. 10—Exponential Relationships Between the Lives of Various Electric Resistor Alloys.

showed a growth of 0.008 inch per foot which was greater than any of the experimental alloys except 10 per cent cobalt. The alloys with 2.5 and 5 per cent aluminum which had shown promise from other properties showed 0.001 and 0.005 inch per foot growths, respectively, and are rated unfavorably on the basis of growth. Short heating tests such as 6 hours at 1090 degrees Cent. (2005 degrees Fahr.) and 2 hours at 1315 degrees Cent. (2400 degrees

Fahr.) did not show any growth in the experimental alloys but did show a growth of 0.08 inch per foot in the iron-chromium-aluminum alloy.

The results of bend tests on specimens which had been heated 6 hours at 1090 degrees Cent. (2005 degrees Fahr.) and 2 hours

Table VII
Results of Growth Tests at 1040 Degrees Cent. (1900 Degrees Fahr.)

Alloy	Growth-in./ft.	Alloy	Growth-in./ft.
2.5 Al	0.001	5.0 Cb	0.003
5.0 Al	0.005	10.0 Cb	0.002
2.5 Co	0.001	80 Ni-20 Cr	0.001
5.0 Co	0.004	37.5 Cr-7.5 Al	0.008
10.0 Co	0.009	25 Cr-5.5 Al-3.5 Co	0.000
2.5 Ti	0.000	25 Cr-5.0 Al-3.0 Co	0.000
5.0 Ti	0.001	25 Cr-4.5 Al-2.5 Co	0.001
2.5 Cb	0.001		

at 1315 degrees Cent. (2400 degrees Fahr.) are shown in Table VIII. It is obvious that the experimental alloys have retained their ductility after this heating, while the iron-chromium-aluminum and iron-chromium-cobalt alloys are very brittle at room temperature. The experimental alloys also remained ductile after heating 100 hours at 1040 degrees Cent.

Table VIII
Results of Repeated 180-Degree Bend Tests Made on Specimens Heated to 1315 Degrees Cent. (2400 Degrees Fahr.)

Alloy	No. of 180° Bends	Alloy	No. of 180° Bends
2.5 Al	3.5	2.5 Cb	4.5
5.0 Al	4	5.0 Cb	2.5
2.5 Co	3.5	10.0 Cb	2
5.0 Co	6	80 Ni-20 Cr	4.5
10.0 Co	8	37.5 Cr-7.5 Al	0
2.5 Ti	3	25 Cr-5.5 Al-3.5 Co	0
5.0 Ti	6.5		

Conclusions

1. The 2.5 and 5 per cent aluminum alloys had the highest yield strengths, tensile strengths, and hot hardness values by a considerable margin up to 800 degrees Cent. (1470 degrees Fahr.). At 1000 degrees Cent. (1830 degrees Fahr.) these alloys had lost these advantages. The aluminum alloys were low in ductility at 600 and

800 degrees Cent. (1110 and 1470 degrees Fahr.). The electrical resistivity at 20 degrees Cent. of these alloys was 26 per cent higher than the commercial 80 nickel-20 chromium alloy used as a base for comparison. Increased life at 1175 and 1260 degrees Cent. (2150 and 2300 degrees Fahr.) was noted for these alloys over the commercial 80 nickel-20 chromium alloy.

2. Of the columbium alloys, the 10 per cent alloy was the best, being next to the aluminum alloys as regards elevated temperature tensile properties up to 800 degrees Cent. The electrical resistivity at 20 degrees Cent. of this alloy was 18 per cent above that of the commercial 80 nickel-20 chromium alloy.

3. The 2.5 and 5 per cent columbium and titanium alloys had similar properties (except the hot hardness of the 5 per cent titanium alloy as noted). Up to 400 degrees Cent. (750 degrees Fahr.) the tensile strengths were slightly less than for the 80 nickel-20 chromium alloy, but at 600 to 1000 degrees Cent. (1110 to 1830 degrees Fahr.) were slightly higher. Small increases in resistivity at 20 degrees Cent. compared with the 80 nickel-20 chromium alloy were found.

4. The cobalt alloys had the lowest properties of the experimental alloys as regards resistivity at 20 degrees Cent. and yield strengths, tensile strengths, and hot hardness up to 800 degrees Cent. (1470 degrees Fahr.).

5. All of the alloys, with the exception of the aluminum alloys, had good ductility (elongation in ½ inch) up to 1000 degrees Cent. (1830 degrees Fahr.).

6. The experimental alloys (except 2.5 per cent titanium) showed growths of 0.001 to 0.009 inch per foot on heating 100 hours at 1040 degrees Cent. (1905 degrees Fahr.) but retained their cold bending properties after heating at 1315 degrees Cent. (2400 degrees Fahr.) for short periods of time.

7. The correlation between the hot hardness and elevated temperature tensile strength of the alloys was good with the exception of the 5 per cent titanium alloy.

Acknowledgments

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DISCUSSION

Written Discussion: By George F. Comstock, metallurgist, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

The subject chosen for investigation by Messrs. Sanford and Harder is an interesting one, and the results obtained should be of value to those concerned with the nickel-chromium wire industry. Although the data in general are well presented by the tables and curves, the text of the paper in some instances seems open to criticism. One rather striking omission in a paper of this kind is the absence of chemical analyses of the alloys investigated. It also seems rather strange to designate alloy No. 12 as a 10 per cent columbium alloy, when the columbium added was not over 8.6 per cent, and 100 per cent recovery is not indicated or claimed. Would it not be preferable to call this an 8.6 per cent alloy, and similarly to call the other alloys what they really are?

The columbium alloys all received appreciable additions of iron, silicon,

etc., and it is unfortunate that the contents of these elements are not given for all the alloys. The silicon content in No. 12 for instance may have had an important effect on its properties. This alloy also apparently contained 8 to 10 per cent less nickel than any of the others, which would seem worth noting.

In the abstract and conclusions very little attention is given to ductility, and further comment from the authors would be appreciated as to whether this property of ductility at high temperature is not of considerable importance in an electrical resistor. The aluminum alloys, which were superior in several respects, were very much lacking in ductility at 600 and 800 degrees Cent., while the titanium alloys showed better ductility than any of the others at those temperatures as well as at room temperature. The superior ductility of the titanium alloys would seem to constitute a noteworthy distinction between them and the others.

Other favorable aspects of the titanium alloys which may be discovered from the data, although they are not brought out by the authors in the text or conclusions, are that they showed less growth at high temperature than the alloys containing aluminum, cobalt, or columbium, and in general better capacity for repeated bending than any of the other alloys except those with cobalt. According to Table VII the growth of the titanium alloys as a class compared favorably with that of plain nickel-chromium, and the authors' statement to the contrary requires correction. The superior resistance to bending of the 5 per cent titanium alloy as compared with the alloys containing 5 per cent aluminum or columbium is interesting in Table VIII, and is presumably a result of the superior ductility conferred by titanium.

In view of the high strength and high temperature life of the aluminum alloys, and the superior ductility and growth resistance of the titanium alloys, an investigation of similar alloys containing both aluminum and titanium should be worth while. I hope the authors will extend this research in that way so that we may be favored with further interesting data on these alloys.

Written Discussion: By Erich Fetz, research metallurgist, Wilbur B. Driver Co., Newark, N. J.

The investigators are to be congratulated for their excellent contribution to the meager knowledge to be found in the international literature on the 80 per cent nickel-20 per cent chromium type of alloys. While there are some German and British publications on the subject, the Battelle investigation represents the only published American research work on the effect of chemical analysis on the physical properties of 80-20. This lack of publication, however, bears no relation to the actual amount of research work carried out in this country, which is tremendous. The production of high grade 80-20 has become the specialty of a few American producers who have disclosed some of their research activity in the patent literature.

I have had the opportunity of perusing Sanford and Harder's manuscript and I am greatly impressed by their bold approach to and noteworthy results of their investigation. The Battelle alloys are interesting insofar as the "substantial additions" of cobalt, titanium, columbium and aluminum exceed the maximum addition of any element deliberately added to commercial 80-20. As to the nature of their additions, we would have probably been very

skeptical if we were consulted about the possibility of melting in an open crucible and working 80-20 alloys containing say 5 per cent titanium or aluminum or even 10 per cent columbium. That is the reason the investigators' work deserves the commendation, "a bold attack."

Sanford and Harder are justified in emphasizing the favorable results obtained with their 2.5 per cent aluminum alloy. From a melter's viewpoint, the addition of several per cent of aluminum presents a most unpleasant undertaking, but 2.5 per cent aluminum seems to be a reasonable limit. This alloy may deserve serious consideration in two regards, i.e., as a room temperature resistance material and as a high temperature resistor alloy.

By diluting pure 80-20 with iron, the resistance increases from 615 ohms per c.m.f. to about 650 ohms per c.m.f. at the 60-15 composition and then drops again on adding more iron. Owing to their favorable working properties, a certain amount of these nickel-chromium-iron alloys are used as cold resistor material and many attempts have been made to further increase the resistance of this nickel-base alloy. However, considerable difficulty is encountered when raising the resistance beyond the 700 ohms per c.m.f. limit. Solid solution hardness and work hardening increase to a prohibitive extent around 750-800 ohms per c.m.f. It is surprising that the authors measured a resistance of 825 ohms per c.m.f. on the 2.5 per cent aluminum and, incidentally, on the 5 per cent aluminum alloy, too. The company with whom the writer is associated aimed at a 2.5 per cent aluminum alloy some years ago but the resistance was only 725 ohms per c.m.f. It is surprising that the hardness of 280 Brinell for the 2.5 per cent aluminum Battelle alloy is the same as for the 5 per cent aluminum alloy, while our 2.5 per cent aluminum alloy was softer by over 100 Brinell.

The strength tests at elevated temperatures are the backbone of the Battelle investigation. It is interesting that the strength at elevated temperatures is greater the higher the room temperature strength. I observed a similar effect in dynamic hardness tests on austenitic steels. The close interrelation between hardness and tensile strength seems to be significant from a practical point of view because it is much easier, cheaper and more efficient to perform hardness tests than tensile tests.

I wonder whether the speaker has any explanation in respect to the loss of ductility around 600 degrees Cent.? It may be rather ungrateful to critically discuss the life test results. After all, it must be left to the discretion of any independent research worker to decide on the scope of his work and in this case it was the elevated temperature mechanical properties. However, since the bulk of commercial 80 per cent nickel-20 per cent chromium goes into the resistor wire application it cannot be denied that there is a particularly great interest in life at elevated temperatures. The investigators have modified the Hoyt and Scheil test introduced for iron-chromium-aluminum, partly adopted features of the A.S.T.M. method used for nickel-chromium and partly introduced their own ideas. In order to make reliable comparisons with other data and to fully appraise the value of their findings, further details on the testing conditions should be given. The comparison with a commercial 80-20 alloy represents a rather untrustworthy basis. I wonder what wire gage and test length has been applied; whether the test was carried out at constant

temperature or constant voltage; what kind of breaking-in or aging treatment has been applied. The tensile tests refer to material in three different wire gages. Does the same hold for the life tests?

The investigators used a load of 35 pounds per square inch as specified by the A.S.T.M. method for 0.025-inch wire, while in the Hoyt and Scheil test the wire of 0.125-inch diameter is even prevented from sagging by some counterweights. It is obvious that the testing results from both methods cannot be compared. This should be borne in mind when consulting Fig. 10 which plots "useful life" of iron-chromium-aluminum and nickel-chromium against testing temperature. The "useful life" has been determined in two entirely different fashions and the illustration only brings out the exponential nature of the life-temperature relation.

The experimenters report nine life tests which bear out the difficulties in testing life at extreme temperatures. For instance, at 1175 degrees Cent. the 2.5 per cent cobalt alloy yields a slightly longer life than the 2.5 per cent aluminum alloy. At 1260 degrees Cent. the cobalt alloy burnt out after 18 hours, while the 2.5 per cent aluminum alloy was still going after 54 hours. In my company, thousands of life tests have been carried out and it was found that there are very many factors affecting life and that there is no simple relationship between chemical analysis and life.

By comparing the 2.5 per cent aluminum alloy with commercial 80-20 the conclusion is drawn that aluminum has a life-extending effect. This agrees qualitatively with results of investigations in my company.

Our quantitative A.S.T.M. tests show that a maximum beneficial effect of aluminum is obtained in a ¾ per cent aluminum alloy while above about 1 per cent aluminum the alloys show a shorter life to 10 per cent resistance increase but the total life to burn-out continues to increase.

It was obvious that the 2 per cent aluminum alloy owed its short "useful life" to 10 per cent resistance increase to sagging. This reduced the cross sectional area and increased the resistance. By extrapolation one would expect the effect of growth or creep would become more pronounced at say 2.5 or 5.0 per cent aluminum, but the investigators' findings are in disagreement with this deduction, although they found in their creep tests the aluminum alloys to be "unfavorable on the basis of growth." In principle, both Battelle and Wilbur B. Driver Company have found the life-extending effect of aluminum and this finding contradicts earlier establishments by Smithells and co-workers who state that 0.5 per cent aluminum does not affect life and that 1 per cent reduces it. These contradicting statements may be due to differences in the life testing methods. The unfavorable, or at least indifferent, effect of titanium and columbium on the life of 80-20 is in agreement with findings in my company.

The remarkably long life of the 2.5 per cent cobalt alloy, to which no life-extending additions except the deoxidizers have been given, represents a distinct surprise and requires corroboration.

It has been pointed out by this writer that the aluminum-containing Battelle alloys deserve serious consideration from several points of view. The data reported however do not agree with former, less favorable results obtained by the Wilbur B. Driver Company. Sanford and Harder were kind enough

to release samples of their experimental alloys for supplementary testing of life according to the standard A.S.T.M. method, electrical resistance and chemical analysis.

The as-received wires had different diameters. The aluminum, titanium and columbium-bearing alloys were 0.102 inch in diameter, the three cobalt-containing alloys were 0.091 inch thick and the commercial alloy 0.081 inch. The accelerated A.S.T.M. life test method specifies a wire diameter of 0.025 inch. The Battelle alloys were, therefore, drawn in standard Brown and Sharpe gages to this size in tungsten carbide and diamond dies. No difficulties were encountered with the commercial cobalt, titanium, and 2.5 and 5 per cent columbium alloys. The alloy with highest columbium content broke twice on its way down. More difficulties were encountered with the aluminum-containing alloys which strain-harden rapidly and in view of their considerable initial strength require intermediate annealings.

All 0.025-inch wires were strand annealed in hydrogen at 1750 degrees Fahr. at a speed of approximately 32 feet per minute. The annealed wires were tested for resistivity in 1-foot lengths in a Wheatstone bridge. The electrical resistance values in Table I are somewhat lower than those determined by Sanford and Harder. The maximum resistance of 807 ohms per c.m.f. was measured on one of the aluminum-bearing alloys. Chemical analysis showed 4.04 per cent aluminum in solid solution. The second aluminum-bearing alloy has a resistance of 782 ohms per c.m.f. and contains 3.82 per cent aluminum per analysis. It thus could not be confirmed that an 80 per cent nickel-20 per cent chromium alloy in which 2.5 per cent nickel is replaced by 2.5 per cent aluminum has a resistivity of 820 ohms per c.m.f. This had been seriously doubted as brought out in the discussion, on the basis of previous experiments. However, two alloys of 77.5 per cent nickel, 20.0 per cent chromium, 2.5 per cent aluminum were melted in a high frequency induction furnace. It is important to stir in the aluminum vigorously as it tends to stay at the melt surface due to its low specific gravity. An incompletely mixed alloy shows considerable variations in electrical resistance. Sections from a $\frac{5}{16}$-inch U-finger were cold-rolled and drawn to 0.025-inch diameter wire. After annealing at 1750 degrees Fahr. a resistance of 687 and 685 ohms per c.m.f. was measured on these alloys. A further melt of 75 per cent nickel, 20 per cent chromium, 5 per cent aluminum yielded 807 ohms per c.m.f. on a section of a finger sample which was converted into 0.025-inch wire with considerable difficulties. The 4 to 5 per cent aluminum-containing alloy is attractive from a resistance viewpoint; however, its manufacturing difficulties are a serious handicap.

Our results do not agree completely with those of Battelle.

The life tests were carried out in accordance with the A.S.T.M. Accelerated Life Test Method, details of which may be found elsewhere.[1] The 0.025-inch wires were tested at 1950 and 2050 degrees Fahr. These tests are performed at constant voltage while Sanford and Harder applied a constant temperature. All of the experimental alloys were life tested, while Battelle had selected only a few alloys.

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[1]Standard Accelerated Life Test for Metallic Materials for Electrical Heating. A.S.T.M. designation B76-36, A.S.T.M. Book of Standards, Part I, 1936, p. 734.

The experimental results are presented in Table II (1950 degrees Fahr.) and Table III (2050 degrees Fahr.). The shortest life was obtained on the nickel-chromium alloys containing titanium which, incidentally, discolored in the strand annealing furnace. The conclusion appears justified that titanium, which formed a poorly adhering oxide coating, drastically reduces life. The

Table I
Electrical Resistance

Alloy No.	Nominal Alloy Additions Per Cent	Chemical Analyses by W. B. Driver Co. Per Cent	Electrical Resistance Battelle on 0.102, 0.091 and 0.081 in. Wire Ohms/c.m.f.	Determined by W.B.D. Co. on 0.025 in. Wire Ohms/c.m.f.
1	2.5 Aluminum	3.82 Aluminum	820	782
2	5.0 Aluminum	4.04 Aluminum	820	807
4	2.5 Cobalt		625	607
5	4.8 Cobalt		611	594
6	9.1 Cobalt		611	590
7	2.5 Titanium	1.93 Titanium	733	718
8	4.8 Titanium		706	696
10	2.5 Columbium		693	663
11	4.7 Columbium		682	665
12	8.6 Columbium 1.2 Silicon		766	750
13	Commercial 80-20	1.85 Manganese	652	656

same holds for the alloys containing up to 5 per cent columbium. A somewhat longer life was obtained in the alloy containing the maximum columbium addition of nominally 8.6 per cent columbium. Whether the relatively long life is attributable to the high columbium content is doubtful.

This alloy contains not less than 1.20 per cent silicon. Silicon has been known for a long time to increase the oxidation resistance of metals and alloys, in general, and the life of nickel-chromium alloys in particular[2, 3]. It is possible that the 8.6 per cent columbium alloy owes its long life to the high silicon content. The introduction of 0.65 per cent titanium may complicate this case furthermore.

Relatively good life was also obtained on the cobalt-bearing alloys. The 2.5 per cent and 5 per cent cobalt-containing alloy yield about the same life. The shorter life of the 10 per cent cobalt alloy is surprising.

The greatest amount of interest is naturally attracted by the aluminum-bearing alloys for which, in the special life test devised by the authors, "increased life was noted over the commercial 80 nickel-20 chromium." According to Tables II and III, the life extending action of aluminum is apparent. However, the "useful life" specified by the A.S.T.M. method as the life to 10 per cent resistance increase is comparatively short and is notably shorter than that of the commercial alloy used for comparison. The aluminum-bearing

[2]C. T. Smithells, S. V. Williams and E. T. Grimwood, "Melting Nickel-Chromium Alloys in Hydrogen." *Journal*, Institute of Metals, Vol. 46, 1931, p. 443-455.

[3]W. Hessenbruch and W. Rohn, "Hochwertige Chrom-Nickel-Legierungen und deren Lebensdauerprüfung," "Heraeus Vacuum-Schmelze 1923-1933," Verlag G. M. Albertis, Hanau, p. 247-289.

samples are subject to considerable creep and warping. The wire temperature falls off markedly at an early stage of the test resulting in a long life to burnout. The above described properties of the aluminum-containing 80-20 are not considered as assets in the light of the A.S.T.M. testing method, which method simulates the application of nickel-chromium in electrical appliances. The A.S.T.M. life tests are discontinued after the test wire has increased 10 per cent in resistance.

Table II
Life at 1950° Fahr. According to A.S.T.M. Method

Alloy No.	Alloy Feature Per Cent	Electrical Input After 24 Hrs. Aging Period Amps.	Watts	Resistance Increase at Burnout, %	Useful Life (10% Resistance Increase or Less) in Hrs.	Life to Burnout in Hours
1	2.5 Aluminum	10.75	153	26.5	106	720**
2	4.8 Aluminum	10.65	146	20.2	152	720***
4	2.5 Cobalt	11.40	152	8.8	91	91
5	5.0 Cobalt	11.40	148	1.8	96	96
6	10.0 Cobalt	11.50	150	14.5	39	67
7	2.5 Titanium	10.05	147	13.3	?	6
8	5.0 Titanium	10.55	141	2.8	16.5	16.5
10	2.5 Columbium	11.20	154	0.2	43	43
11	5.0 Columbium	11.10	163	6.0	27.5	27.5
12	10.0 Columbium	10.30	151	13.7	110	187
13	Commercial 80-20	11.30	159	9.5	199*	199

*Mean value of 3 tests.
**Removed after 720 hrs. at 26.5% resistance increase. Wire temperature had dropped from 1950° Fahr. to 1706° Fahr.
***Removed after 720 hrs. at 20.2% resistance increase. Wire temperature had dropped from 1950° Fahr. to 1706° Fahr.

The aluminum-containing samples showed a behavior previously observed on similar alloys and characterized in the foregoing discussion. It appears that the difference in the life testing conditions are responsible for the discrepancy in the testing results obtained by Sanford and Harder and by the A.S.T.M. method. The increased resistance toward oxidation due to addition of substantial amounts of aluminum to 80 per cent nickel-20 per cent chromium is brought out by both life testing methods.

It should not be overlooked that Battelle tested the commercial alloy as 0.081-inch diameter wire, while the aluminum-containing alloys had a diameter of 0.102 inch.

The commercial alloy used for comparison shows an unusually short life. It apparently corresponds to the state of the art of several years ago. The remarkable advances since that time are described at length elsewhere.[3, 4]

A few chemical analyses were made, the results of which are presented in the third column of Table I. It is generally known that certain elements such as titanium, aluminum, calcium, etc., are subject to considerable losses in melting which point is brought out by the few check analyses made. The

[4]F. E. Bash, "Estimating Life of Electrical Heating Elements," METAL PROGRESS, Vol. 33, No. 2, p. 143-147.

calcium content of the experimental Battelle alloys varies between 0 per cent and 0.038 per cent so that the alloys are not strictly comparable as to the effect of aluminum, titanium, columbium and cobalt on the life.

The life testing of resistor wires is considered to be one of the most complex metallurgical problems. The chemical composition is only one of the many factors determining the longevity of nickel-chromium alloys.[3] This

Table III
Life at 2050° Fahr. According to A.S.T.M. Method

Alloy	Alloy Feature Per Cent	Electrical Input After 24 Hrs. Aging Period Amps.	Watts	Resistance Increase at Burnout, %	Useful Life (10% Resistance Increase or Less) in Hrs.	Life to Burn-out Hours
1	2.5 Aluminum	11.40	173	22.9	40	120**
2	5.0 Aluminum	11.30	167	35.0	97	624***
4	2.5 Cobalt	12.45	178	3.4	40	40
5	5.0 Cobalt	12.50	184	2.0	35	35
6	10.0 Cobalt	12.15	162	16.0	19	33
7	2.5 Titanium	10.30	153	8.3	7.25	7.25
8	5.0 Titanium	10.70	164	over 10%	4.25	7
10	2.5 Columbium	11.20	166	4.7	4.5	4.5
11	5.0 Columbium	10.60	158	10.0	19	19
12	10.0 Columbium	10.45	162	8.4	52	52
13	Commercial 80-20	12.05	174.5	5.9	154*	154

*Mean value of 2 tests.
**Removed after 120 hrs. at 22.9% resistance increase. Wire temperature had dropped from 2050° Fahr. to 1864° Fahr.
***Removed after 624 hrs. at 35% resistance increase. Wire temperature had dropped from 2050° Fahr. to 1775° Fahr.

renders it difficult to draw conclusions regarding the effect of individual elements on the life of 80 per cent nickel-20 per cent chromium if all the other factors are not equal. Furthermore, the effect of individual elements on the life of 80-20 may be obliterated to a far-going extent in the presence of other elements.

V. N. Krivobok:[5] As is customary in our society the authors of this very interesting paper have signified that they welcome discussion. In studying the paper prior to the meeting and also listening to the discussion of the same by Mr. Fetz one very worthwhile fact was brought to our attention. I have in mind the observation that during high temperature tests certain metals show, within a certain temperature range, a drop in ductility as measured by elongation. In the course of a recent investigation I have myself observed similar phenomena and tried to uncover the underlying reasons. I am taking the liberty to describe these observations.

May I state first of all that the compilation of available data on the mechanical properties of steels and alloys at high temperatures are often found to be in discrepancy. It is especially noticeable in the given values for

[5]Professor of metallurgy, Carnegie Institute of Technology, Pittsburgh, and associate director of research, Allegheny Ludlum Steel Corp., Brackenridge, Pa.

elongation and reduction of area, although the tensile strength may also vary. The first thought that may come to one's mind is that such discrepancies are caused by the conditions of experimental procedure. This explanation will, however, have to be abandoned for the following reasons. Working not so long ago on the high temperature properties (as measured by the so-called short time tests) of some of the alloys, I was indeed surprised to find quite large variation which may be obtained in, shall we say, elongation values, obtainable in alloys of similar composition and under absolutely identical conditions of testing. A careful examination of broken pieces revealed wide differences in the type of fracture and it was only to be expected that the values for elongation were quite different. In certain cases the fracture was very much like that of an end of a sharpened pencil; gradual smooth reduction ending almost in a point. In other cases the fracture showed only little cross sectional reduction and emanating from the broken end were noted a number of relatively fine cracks extending for quite some distance from the fractured end. Microscopic examination of the material immediately gave clue to this observation, namely that the type of fracture was dependent upon the grain size of an alloy, in this case as it happened, of the austenitic type. The first described fracture, namely smooth pointed one, is invariably found in the alloy of fine grain size. It should be added that the composition of the alloy apparently exercises some influence, that is the described phenomenon may be more pronounced in one alloy than in the other. Pursuing this investigation in accordance with more carefully considered plan I find that the values for elongation and for the reduction of area may be changed within wide limits by the mere alteration in the grain size; similarly, we may change the type of fracture—as you would expect. On the other hand the tensile strength seems to be but little affected by the grain size; for example, while values for elongation could be halved, by mere increase in grain size, the tensile strength is decreased only something like 3 to 5 per cent.

Authors' Reply

The authors wish to thank those who discussed this paper for their very helpful contribution.

In reply to Mr. Comstock, we agree with him that chemical analysis of the materials investigated, and data on the recoveries of the alloys added, would have been very desirable.

Ductility at elevated temperatures, if concomitant with good elevated temperature tensile strengths, is a desirable property of electrical resistor materials. With such a combination of properties, longer spans of unsupported resistors may be used, and the material should be capable of withstanding more abuse in service without breakage occurring.

While the growth tests which were made were inadequate for a complete appraisal of the growth characteristics of the materials, the results did indicate that the titanium alloys, as a class, were less subject to growth than the aluminum, cobalt or columbium alloys, and compared favorably with the 80 nickel-20 chromium alloy. However, the 2.5 per cent aluminum, cobalt, and columbium alloys showed growths of the same order as the titanium alloys

and it was only the higher aluminum, cobalt and columbium alloys which showed the increased growths. As suggested by Mr. Comstock, it would be interesting to know the combined effects of aluminum and titanium.

Mr. Fetz's comments on the work which has been done along similar lines by his company are particularly appreciated. We cannot make comparison with his data since we did not test alloys containing less than a nominal 2.5 per cent addition of aluminum. It is gratifying to note that the results of Mr. Fetz's company regarding the life of 80-20 alloys with aluminum, titanium and columbium are, at least qualitatively, in agreement with ours.

As to why the aluminum alloys lose so much of their ductility in the range from 600 to 800 degrees Cent., we can give no answer. Dr. Krivobok's comments regarding the loss of elongation at certain temperatures for heat resisting alloys and some of the possible causes are interesting and may contain the answer to the low ductility of the aluminum alloys at 600 to 800 degrees Cent. Our tests showed a difference in the type of fracture in the range of 600 to 800 degrees Cent. but no coarsening of the grain was noted.

Our life tests were made at constant temperature using photoelectric cell control and 12-inch specimens. The specimen diameters were the same as in the tensile tests.

We wish to thank Mr. Fetz and his company for the standard A.S.T.M. life tests, the electrical resistivity measurements, and the chemical analyses which they made on our alloys.

When the alloys were sent to Mr. Fetz it was stated that it was not known whether the aluminum alloys were from the same heat or not, because of a mix-up of these materials after the completion of our tests. His analyses of 3.82 and 4.04 per cent aluminum indicate that both samples were from the heat with the 4.8 per cent nominal addition of aluminum and his results should be viewed on that basis.

The small discrepancies between his resistivity measurements and ours can probably be accounted for by the fact that he annealed the specimens in hydrogen, whereas we annealed them in air with a resultant thin oxide film which would increase the resistance slightly. His resistance values check more closely with those tabulated below, which we made on the alloys before annealing in air at 1000 degrees Cent.

Alloy	Ohms/c.m.f.	Alloy	Ohms/c.m.f.
2.5 Al	792	2.5 Ti	723
5.0 Al	805	5.0 Ti	705
2.5 Co	602	2.5 Cb	667
5.0 Co	590	5.0 Cb	674
10.0 Co	592	10.0 Cb	760

In connection with his resistance values of 685 and 687 ohms per c.m.f. on the 77.5 nickel, 20 chromium, 2.5 aluminum heat which he made up, it would be of interest to know the actual aluminum content by analysis, as our results on the 2.5 per cent aluminum alloy (2.33 per cent aluminum by analysis) were of the same order as for the 5 per cent aluminum alloy.

The results of Mr. Fetz's life tests by the standard A.S.T.M. method are of particular interest in that the results are in good general agreement with ours as to the life-extending properties of aluminum additions to 80-20, even

though the life test methods used were considerably different and at different temperatures.

A.S.T.M. standard B76-36 does not seem to specify that the life to 10 per cent resistance increase shall be considered as the "useful life," nor that the test shall be discontinued after the test wire has increased 10 per cent in resistance. On the contrary, the standard specifically calls for testing to burnout by supplying a place for the burnout life in hours in the record form specified. The appendix to the standard states that the life to 10 per cent resistance increase has been considered as the "useful life" in some instances, but that in other cases the "useful life" extends to burnout, depending on the application of the resistor.

Mr. Fetz states that the commercial 80-20 used for comparison "corresponds to the state of the art of several years ago." This material was purchased in 1937 at the time this work was being done and presumably corresponds to the state of the art at that time. It is to be regretted that Mr. Fetz did not include in his discussion life test values of current 80-20 production for comparison.

Bash (METAL PROGRESS, Vol. 33, No. 2, p. 143) shows a total A.S.T.M. life to burnout of about 400 hours at 2050 degrees Fahr. for what is presumably the best 80-20 production at that time (1938) but does not indicate the life to 10 per cent increase in resistance nor the temperature of the test wires just before burnout. The 5 per cent aluminum alloy had not burned out when removed after 624 hours at 2050 degrees Fahr. in Mr. Fetz's tests. For some applications this represents a definite improvement over an alloy which burns out in 400 hours.

The major criticism of the A.S.T.M. standard life test is brought out very well in the footnotes to Mr. Fetz's Tables II and III, where the wire temperatures at the completion of the tests had dropped from 186 to 275 degrees Fahr. below the initial test temperatures of 1950 and 2050 degrees Fahr. A constant temperature life test such as we used is much more drastic than the A.S.T.M. life test at constant voltage, in which the wire temperature drops continuously as the wire resistance increases after the first 24 hours.

It is believed that Mr. Fetz overestimates the difficulties of processing the aluminum-bearing 80-20 alloys. While the aluminum alloys did require more careful handling during forging, rolling and swaging, no really serious difficulties were encountered.

GRAPHITIZING RATE AND NODULE NUMBER

By H. A. Schwartz and Martin K. Barnett

Abstract

The authors have investigated the question whether graphitizing rate is proportional to nodule number. Only a qualitative confirmation was obtained. In general graphitizing rate increases as a fractional power of nodule number except under conditions so controlled that only moderate variations in nodule number are possible.

Introduction

THE mechanism of the graphitizing reaction is now sufficiently understood (1), (2), (3)[1] so that there is general agreement that nodule number is an important factor in determining graphitizing rate. Methods for computing nodule number per unit volume without assuming uniformity of size are also available (4), (5).

It is also well known that the nodule number is not solely or primarily a function of chemical composition, but depends also upon the melting method and material and upon heat treatment as has been in part described in the literature (6), (7), (8), (9), (10), (11).

At first glance it would seem from symmetry considerations that the amount of graphite formed per unit time should be proportional to the number of nodules per unit volume. This simple conclusion is not however altogether acceptable on *a priori* grounds without verification. Fick's law is known not to be perfectly reliable in the study of other diffusion phenomena in that the rate of diffusion is not independent of concentration (12). Furthermore, there may be disturbances due to the fact that a temper carbon nodule is not a solid mass of carbon but a sponge. Carbon migration from graphite particles of small radius of curvature to those of larger radius may cause interference. Nor is it perfectly certain that all nodules are capable of growth. If there be a change of atom arrangement as between boydenite and austenite, this would introduce additional complications.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, Dr. H. A. Schwartz is manager of research and Martin K. Barnett is research chemist, National Malleable and Steel Castings Co., Cleveland. Manuscript received March 29, 1938.

Some attempt at a quantitative correlation of graphitizing rate with nodule number therefore seems justified. It is not considered opportune to enter here upon the question of possible control of nodule size.

Experimental Procedure

In connection with certain other investigations there was occasion in this laboratory to follow the time-graphite curves at 900 degrees Cent. (1650 degrees Fahr.) of nineteen white irons of very similar compositions which were known to produce different densities of nodule population. For the general methods of experimentation and for confirmation of the similarity of most such curves, consultation of reference (1) is suggested to avoid lengthy repetition of old material. The nodule number was determined (5) on material in a nearly completely graphitized condition. It is a first approximation to say that graphite forms by an increase in size rather than number of nodules (8). Quite possibly some correction of this concept is required, but so little data have yet been accumulated regarding nodule number that more elaborate treatment cannot yet be attempted.

The average carbon content of the nineteen lots of white iron was 2.58, the average silicon 0.93 and none contained unusual alloys. The choice of this composition was dictated by considerations pertinent to the major investigation, but it is convenient for the present purpose. All the metal was made in commercial melting furnaces and the composition in no case varied by more than 0.03 per cent from the above mentioned average.

For purposes of comparison the metal falls naturally into three subdivisions. The first consists of fourteen heats which can be subdivided according to origin into two groups of seven heats each. Each of the two groups is fairly similar within itself with regard to nodule number and graphitizability but the two differ considerably with regard to these properties. The second subdivision consists of three heats of widely different origin but of rather similar properties. Varying nodule numbers are imposed on these in the laboratory by changes of heating rate. The third subdivision consists of a metal graphitized before and after prequenching.

Experimental Data

The time-graphite curves at 900 degrees Cent. (1650 degrees Fahr.) of the nineteen materials are shown graphically in Figs. 1, 2

and 3. The time scale is logarithmic for a reason which will appear presently. In further elaboration of Fig. 1 the nodule number of the fourteen heats is shown separately in Table I.

Table I

Heat	Nodules per mm.^{3} Nodule No.	Heat	Nodule No.
1	113	8	73
2	739	9	78
3	180	10	103
4	159	11	107
5	194	12	85
6	819	13	133
7	282	14	58
Average	355	Average	91

Evaluation of Results

It is not to be expected in work of this character that perfectly concordant and reproducible results should be obtained. Micrometric measurements such as underly the nodule count have decided limitations of precision and the mathematical postulates underlying the solution of the geometric problems are only first approximations. Although the determination of graphite as a chemical problem is fairly satisfactory, it is still difficult to get altogether satisfactory checks on the amount of graphite formed in a given time. Quite possibly this is due to unknown or uncontrolled variables in even careful graphitization experiments.

Under these circumstances it is desirable to base conclusions, not on a detached study of single experiments, but on comparisons of fairly large groups of observations. With this end in view it seems well to make a comparison between the entire course of the graphite-time curve representing heats 1 to 7 with that of heats 8 to 14 inclusive in Fig. 1 and between the several average graphite-time curves for heats 15 to 17 inclusive of Fig. 2, leaving the two rather extended investigations of metals 18-19 of Fig. 3 for a third comparison.

This raises the question of determining the locus for the several arrays of points involved. A curve was drawn for each group, by inspection, considering that this line should pass, if possible, through the mean value of graphite for each graphitizing time but considering

also that the curves should be similar, that is, that on the chosen logarithmic time scale the curves should be alike in form and displaced from one another parallel to the time scale. The amount of this displacement is then the logarithm of the ratio of the times to secure a

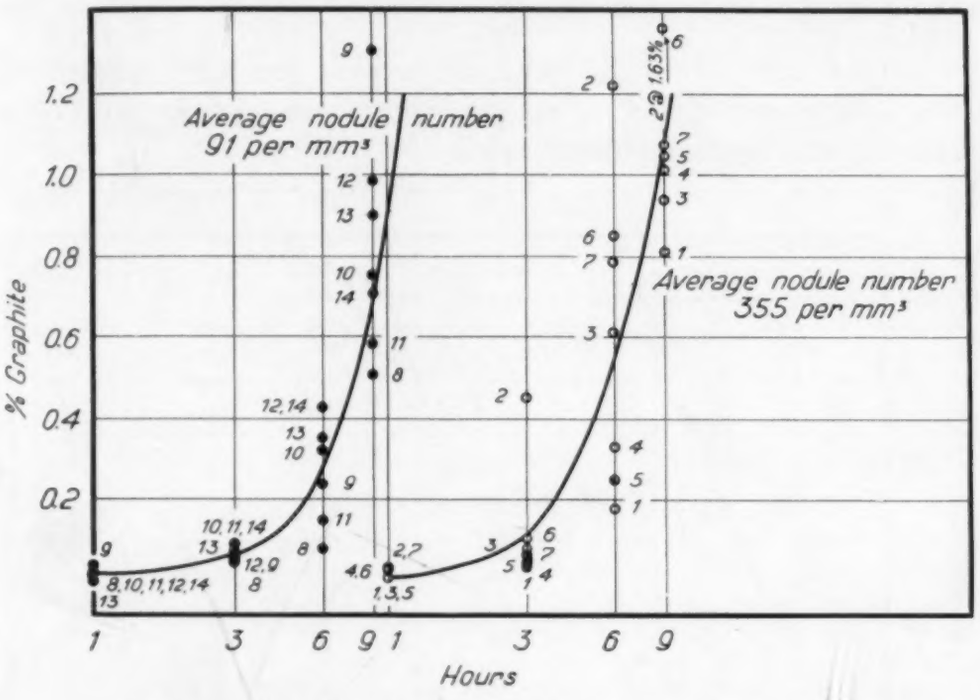


Fig. 1—Time-Graphite Curves at 900 Degrees Cent. (1650 Degrees Fahr.).

given degree of graphitization (amount of graphite since the total carbons are substantially identical) or of the reciprocal of the graphitizing rate. The calculation of the ratio of nodule numbers is merely a matter of division. We thus obtain the data of Table II.

Table II

Fig.	Ratio Nodule No.	Ratio Graphitizing Rate
1	355 ÷ 91 = 3.9	1.4
2	361 ÷ 42 = 5.6	4.0
	546 ÷ 361 = 1.5	1.3
	361 ÷ 125 = 2.9	2.2
	361 ÷ 246 = 1.4	1.4
3	270000 ÷ 630 = 420	12.0

Discussion of Results

Consider the data of Fig. 2 in which the comparison is between identical alloys, in which the nodule number is imposed without any

alteration in the metal. The ratios of "Ratio of Nodule Numbers" to "Ratio of Graphitizing Rates" are $\frac{5.6}{4.0} = 1.4$, $\frac{1.5}{1.3} = 1.2$, $\frac{2.9}{2.2} = 1.3$ and $\frac{1.4}{1.4} = 1.0$, an average of 1.2. Although graphitizing rate does not increase quite as rapidly as nodule number, one might regard this value as confirmation of an at least approximate proportionality of nodule number and graphitizing rate.

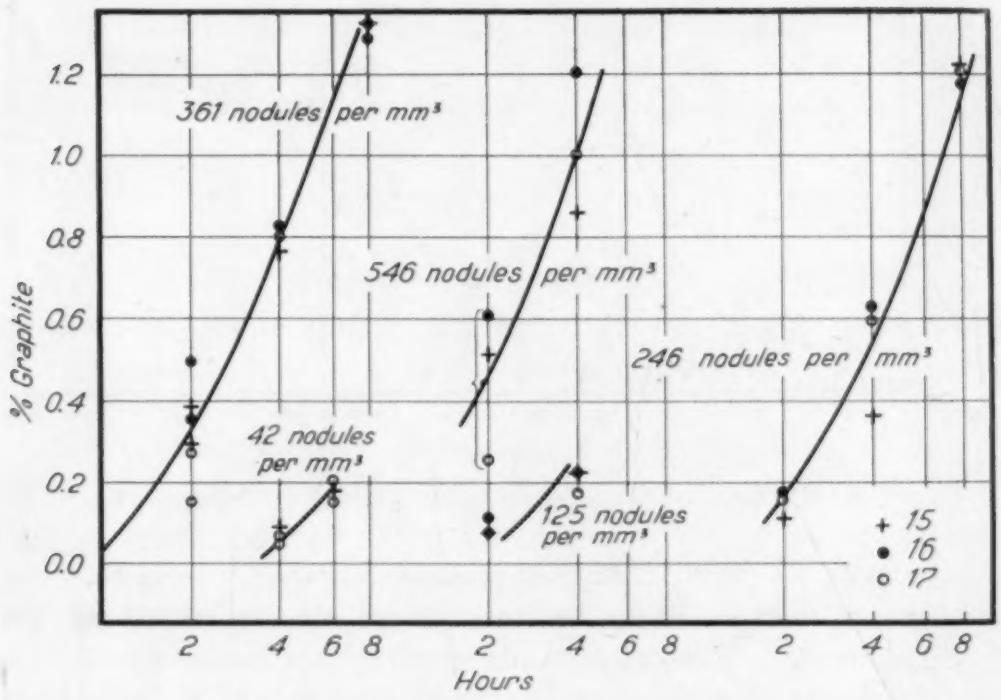


Fig. 2—Time-Graphite Curves at 900 Degrees Cent. (1650 Degrees Fahr.).

If, however, the nodule number in a given metal is enormously increased by drastic prequenching, as in Fig. 3, the acceleration of graphitization is very much less than proportional to the change in nodule number, in fact only one-thirty-fifth the expected amount. The observations are those which would be expected if migratory rate instead of being proportional to the carbon concentration gradient grew less rapid (in proportion to the gradient's steepness) as the steepness of the gradient is greatly increased.

By measuring the distance parallel to the time axis between the points of Fig. 1 from their trend lines and averaging these distances

for all the points* representing a given heat one can determine the relative graphitizing rate of each heat in a group, the rate for the group average being taken as unity.

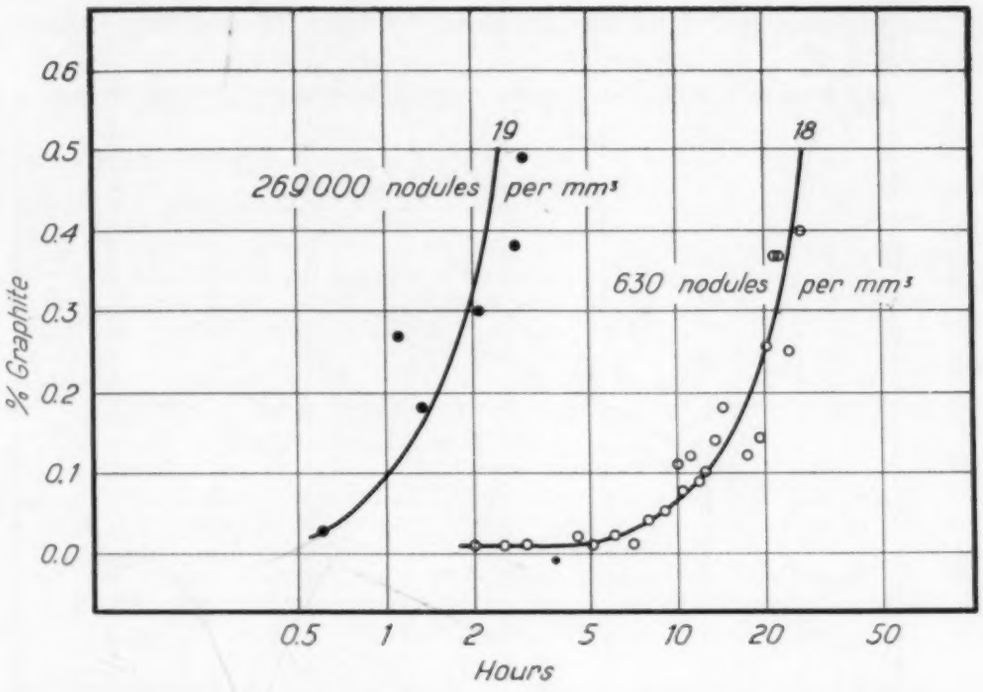


Fig. 3—Time-Graphite Curves at 900 Degrees Cent. (1650 Degrees Fahr.).

The ratio of the nodule number to the average nodule number of the group is readily found from Table I. In Fig. 4 the *relative* graphitizing rate is plotted against *relative* nodule number. The array of points is but poorly represented by a straight line through the origin representing proportionality of graphitizing rate and nodule number, but is much better represented by a curved trend line corresponding to a relationship such as was deduced from Figs. 2 and 3, namely that graphitizing rate increases less rapidly than nodule number and that the effect of an increase in nodule number becomes less and less as the number increases.

The curve shown in Fig. 4 represents the relationship that the graphitizing rate is proportional to the square root of the nodule number. The data of Fig. 3 correspond to the 2.4 power instead of the square. The corresponding powers deduced from Fig. 2 in the order in which the ratios appear in Table II are 1.2, 1.6, 1.4 and 1.0.

*In view of the shape of the trend line it is well to omit as uncertain measurements based on the observations of graphite content after an exposure of one hour.

That deduced from the two groups of Fig. 2 is about 4. Since we know from Fig. 4 however, that each of the two groups within itself corresponds approximately to a quadratic relation of nodule number and graphitizing rate, a better explanation is to say that in the score of nodule number alone the graphitizing rates should have been as

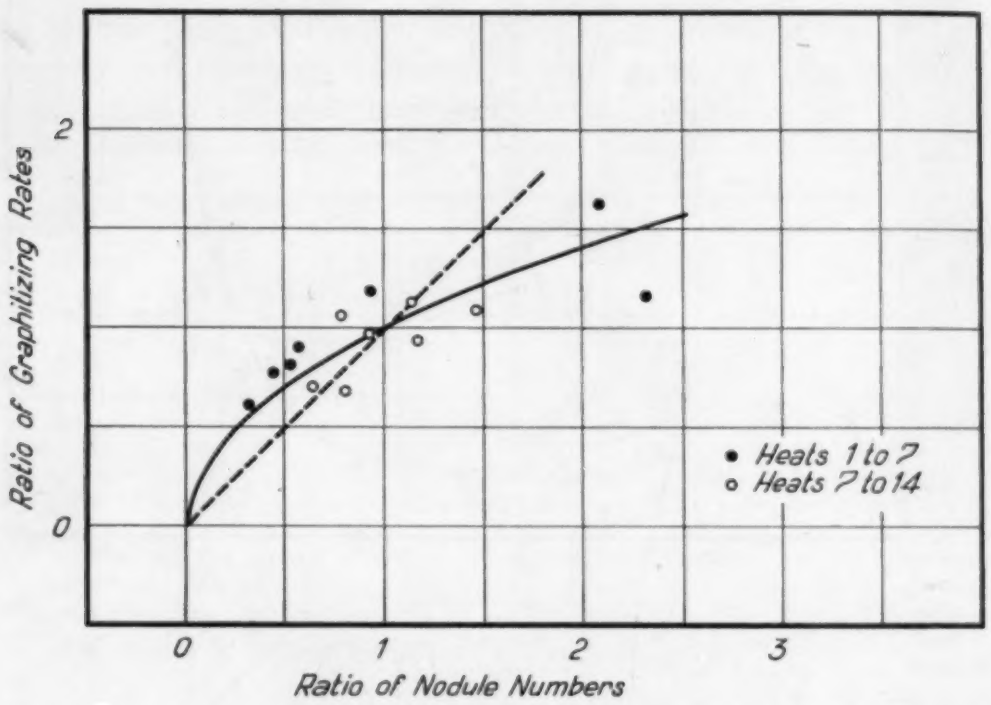


Fig. 4—Curves Showing that the Relationship of Graphitizing Rate is Proportional to the Square Root of the Nodule Number.

4:2 and that the fact that the graphitizing rates are only as 1.4:1 instead of as 2.1 is due to a different migratory rate characteristic of the two groups of alloys.

Conclusions

Generalized conclusions based on a limited amount of information in a largely unexplored field would obviously be indiscreet. As first approximation only we hazard as suggestions:

(1) In general graphitizing rate increases less rapidly than nodule number.

(2) For exactly identical metal and a limited range of nodule number (say from 100 to 500 per mm^3) almost strict proportionality may exist.

(3) For less similar conditions the graphitizing rate is proportional to a fractional power of nodule number which may be as low as 0.4.

(4) Even iron of apparently identical analysis may vary in migratory rate of carbon in a ratio as high as 2:1.

(5) Qualitatively increased nodule number is accompanied by increased graphitizing rate under otherwise similar conditions.

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DISCUSSION

E. C. JEETERS:[1] Why is there such a great rearrangement in the nodule number of the sample selected? For example, four different groups are averaged but in each group there is a wide rearrangement between one and the other.

CYRIL WELLS:[2] Dr. Schwartz and Mr. Barnett have shown that in their

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[2]Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh.

alloys an increased nodule number is accompanied by an increased rate of graphitization under similar conditions of heat treatment, and in this respect their results confirm those of Wells[a] who used high purity iron-carbon alloys in his graphitization studies.

With respect to the conclusion that within a limited range of nodule number there is a strict proportionality between nodule number and rate of graphitization, the present discusser believes that the extent of this limited range depends to some degree on the silicon content of the alloy used. In pure iron-carbon alloys strict proportionality between graphitization rate and nodule number may extend over a considerable range of nodule number. Silicon heterogeneously distributed may also be partly responsible for the authors' observation that graphitization rate increases more rapidly than nodule number and for the different behavior of iron of apparently identical analysis.

I should like to ask Dr. Schwartz one question. Why does he think that if one doubles the number of nodules one should double the rate of graphitization, unless, of course, he assumes that in both cases the nodules are so far apart as not to influence each other?

Authors' Reply

We do not know that we can make any intelligent answer to Mr. Jeeter's question which we take to be "Why are things which are apparently alike still somewhat different in nodule number?" There is a value of 800 and one of 700. They are somewhat exceptional and in the other case they range from a minimum of 73 to a maximum of 133. We have not the slightest idea why that happens unless one goes backward and reasons about all of the things which affect nodule number. We think we are quite safe in the conclusion that the nuclei for these nodules always appear first on the austenite interfaces and therefore any vagary in freezing possibly say due to pouring temperatures which alters the fineness of structure of the freezing pattern is one of many such variables.

We happen to know that aside from this particular performance, for instance, in iron made in a Detroit furnace under rather closely controlled conditions, the amount of oxygen in the atmosphere alters the nodule numbers. The nuclei all form on this interface in various numbers per unit of area at one time and another. We know not why but we suppose these variations that are here tabulated represent the integration of that multitude of variables. It is not altogether uninteresting perhaps to comment here that within these groups the graphitizing rate also bears some general connection to the nodule number; e.g., it is not only the group with 355 nodules per cubic millimeter which differs from the group with 91 but also within each of those groups the graphitizing rate is great or small though not quite so well in agreement because obviously we have not the average of so many results but the general qualitative relation still remains.

As to Dr. Wells' inquiry as to why should two nodules grow twice as fast as one, as far as graphite formation is concerned, we think our concept

[a]Cyril Wells, "Graphitization in High Purity Iron-Carbon Alloys." TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 289.

about that is approximately this. We apologize for repeating material which has been published and is probably more familiar to one who works with it every day than to those who only read it and have no great further occasion to remember it. We must make some sort of simplifying assumption. If we permit an indefinite amount of variation in distribution in what Dr. Wells perhaps calls heterogeneous distribution, the space of these nodules in the same material affects the result. The more of that you permit the less does this initial assumption apply. We will visualize nuclei as being on the corners of cubes in the material. In one case suppose they are on the corners of cubes one unit long and in the other case on the corners of cubes ten units long. Of course they are not nearly so different in most cases. They begin to grow and while they are growing at high temperature they consist of a spheroidal mass of carbon surrounded by austenite, the whole imbedded in an austenite-cementite nuclei. They have a carbon gradient from the cementite saturated solid solution on the outside of the shell to the graphite saturated solution on the inside of the shell. Be the size great or small, until these shells become tangent to one another so that there are areas where the whole outer surface of the shell is not filled up with cementite, the geometry of the problem remains exactly the same and we think the rate of the growth should be the same. As soon as these shells interfere then there is not the "rain" of carbon atoms from all around this sphere but only from the remaining areas of the sphere and the time-graphite curve does show about half graphite formed which is the relation of the volume of the sphere to the volume of the cube.

Now our picture of that is as reliable as the picture represents the ordinary condition. We think nobody maintains that the nodules are exactly so located and, of course, if some of them are close together those things would interfere and distort the curve before much graphite has come out, but also if they are close together that happens when the amount of the graphite affected thereby is small and the curve is not greatly distorted.

We think maybe the best evidence that that concept is somewhere near right is pragmatic in that the empirical curves do correspond to what they ought to on the original postulate. That is the only direct evidence we know about it. We first made the curves several years ago. We made many assumptions as to the possible explanation, assuming things that we thought might be plausible and the above described picture is the plausible thing that fits the quantitative facts. You do not get smooth curves as the astronomer might get. You get curves with a considerable scatter because if you do your experiment twice over you do not literally come out with precisely the same value which is one reason why the principles of graphitization are hard to study just as biological subjects are. You cannot hit the thing exactly on the head. You make many observations and are content with smoothings out. The thing we doubt most about this parabola-shaped curve is whether the bend in that curve is very largely influenced by the weight you give of the very fine-grained material. If you would use a little section of this curve you could represent it by a straight line very nicely. The quadratic curve is the best we could do to fit the entire range of result. We would not swear on a stack of bibles that the thing is all statistically one universe and that we do not have two curves superimposed, one representing one set of the figures and the other another. We

might find some other system could be worked out that would fit better. The difficulty with that is we have not a sufficient multitude of data for one universe which is extremely fine-grained and another universe which is more coarse-grained and the only reason we do not have that is because we have not an indefinite amount of time, an indefinite number of observers, and an infinite amount of patience.

STUDY OF CARBIDE SOLUTION IN HYPOEUTECTOID PLAIN CARBON AND LOW ALLOY COMMERCIAL STEELS

By R. H. Lauderdale and Oscar E. Harder

Abstract

Data of a fundamental nature have been obtained regarding the rate of carbide solution and formation of austenite at temperatures above the Ac_1 in plain carbon and low alloy hypoeutectoid steels.

Production of coarsely spheroidized carbide structures, followed by solution treatments in a lead bath of these structures at various temperatures and time intervals then followed by quenching, made it possible to follow the progress of the carbide solution by microscopic examination and hardness determinations of the quenched specimens.

It has been postulated that the solution of carbides, especially those of low alloy steels, progresses rather slowly at temperatures of normal hardening and grain size determinations and that these undissolved carbides may act to inhibit austenite grain growth. However, the authors have obtained evidence that in low and medium carbon hypoeutectoid steels the carbides go into solution so rapidly at normal heat treating temperatures that the carbides could not possibly be important in the usual grain coarsening experiments. In the higher carbon steels (0.77 and 0.78 per cent carbon) tested, the time for complete carbide solution was much longer and only less definite conclusions could be drawn regarding the effect of undissolved carbides on grain growth. Maximum hardness values in quenched specimens tended to confirm microscopic evidence that solution of the carbides occurred within 10 to 30 seconds at 1600 degrees Fahr. in steels containing 0.40 per cent carbon or less.

AS part of a general study on grain growth characteristics of commercial steels, the present investigation was carried on with the objective of determining the rate of solution and the time necessary for the complete solution of carbides in hypoeutectoid steels at tem-

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peratures within and above their critical ranges. The effect of time at various temperatures on the hardness developed in quenched specimens was also determined. The primary objective was to learn whether carbides in hypoeutectoid steels actually remain undissolved long enough to be effective in inhibiting austenite grain growth.

One of the general theories relating to the austenite grain growth mechanism, expressed by a number of metallurgists, including McQuaid (1),[1] Kenyon and Tobin (2), Herty (3), and Bain (4), is that austenite grain growth may be inhibited by finely dispersed nonmetallic particles such as carbides, nitrides, and refractory oxides. McQuaid (1) postulates that carbides dissolve very slowly at temperatures even above the upper critical temperatures and thereby act as grain growth inhibitors. It has been further suggested by Kenyon and Tobin (2) that spheroidized carbides produced by long subcritical holding treatments in hypoeutectoid steels (0.40 per cent carbon) do not go into solution in as long a holding time as one hour at temperatures as high as 1650 to 1750 degrees Fahr. and therefore may act to inhibit austenite grain growth.

The authors questioned that carbides dissolve slowly in hypoeutectoid steels at temperatures above the Ac_1, especially above the upper critical temperature, and likewise questioned whether this could have much to do with the austenite grain growth inhibition. Under these circumstances it was highly important in a study of grain growth characteristics to know to what extent carbides could function to inhibit the austenite grain growth at various temperatures and especially above the upper critical temperature which would represent commercial heat treating practice. The present investigation was therefore directed to getting definite information on the rate of carbide solution and the time required for complete disappearance of the carbides in several hypoeutectoid steels over a considerable range of temperature. Four of the steels contained small amounts of molybdenum or vanadium and made it possible to obtain some information on the effect of these elements on carbide solubility.

Some of the steels studied were the same as those previously investigated by Dorn and Harder (5) in their study of the relation of pretreatment of steel to austenite grain growth. Much longer subcritical holding treatments than were used by Dorn and Harder were given the steels in this investigation in order to coarsen the carbides and to make the conditions for carbide solution at least as

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

unfavorable as would be encountered in commercial practice. It was considered highly important to determine the effectiveness of carbide particles in inhibiting austenite grain growth in comparison with a grain growth inhibitor "X" such as had been postulated by Dorn and Harder (5).

In this investigation the solution of the carbides was followed by microscopic examination of specimens quenched from various temperatures after various time intervals and supplemented by Rockwell "C" hardness determinations on quenched specimens.

The type of structure representing the most difficult case of carbide solution, i.e., very coarse carbide particles in a ferrite matrix, was studied for it was believed that if the carbides in this type of structure would dissolve rapidly, there could be no doubt that the rate of carbide solution in commercial structures (pearlitic or finely divided or spheroidized cementite) would be much greater.

The results which have been obtained provide more information on carbide solubility and the time required at the holding temperatures to develop full hardness in quenched specimens than they do about austenite grain growth. However, it seems obvious that the very rapid rates found for carbide solubility in steels of about 0.40 per cent carbon or less preclude the possibility of the carbides in such steels having any important effect in retarding the growth of the austenite grains.

Previous Investigations

Few exact data have ever been published on the rate of solution of carbides in hypoeutectoid steels. As far as the authors know, no investigator has studied the solution of such coarse carbide particles as were used in the present investigation, especially in a hypoeutectoid plain carbon or low alloy steel.

McQuaid (1) made a limited investigation of the rate of carbide solution in three aluminum-killed steels of similar analyses to the ones studied in the present investigation. He reported that a steel (0.38 per cent carbon, 0.85 per cent manganese, 0.13 per cent silicon, 0.011 per cent aluminum) in the normalized condition required about 15 minutes at 1500 degrees Fahr. to complete carbide solution and that the same steel spheroidized for 24 hours at 1225 degrees Fahr. required over 15 minutes at 1700 degrees Fahr. to effect complete solution.

R. G. Guthrie (7) made a study of "the importance of the condition of cementite" and although no specific data were presented as to the rate of carbide solution in hypoeutectoid steels, he emphasized the great difficulty with which carbides in the spheroidized condition go into solution at normal hardening temperatures.

Bain (4) investigated several steels of the same analyses, one in the normalized condition and one in the spheroidized condition and brought out the difference in the rate of solution of the carbides in the two types of structures. He heated each steel a short period of time at several temperatures above the lower critical and determined the temperature required to develop the same maximum hardness from each steel by quenching. No conclusions as to the rate of carbide solution can be drawn from Bain's work because he failed to specify the analyses of the steels used and the time the specimens were held at temperature before quenching.

A number of investigators have studied carbide solution in hypereutectoid plain carbon and alloy steels but obviously the results of such investigations cannot be correlated to the present investigation on definitely hypoeutectoid steels.

Materials and Procedure

The chemical compositions of the steels studied are given in Table I which also shows the type of furnace used in their production. The total aluminum contents suggest that five of these steels have had enough aluminum added to have an effect on the grain growth characteristics. In addition, steels "C13" and "B10" are relatively high in nitrogen.

Table I
Chemical Composition of Steels Used in Carbide Solubility Investigation

Lab. No.	C	Mn	Si	P	S	Va	Mo	Cr	N	Total Al	Melting Furnace
C11	0.78	0.24	0.22	0.013	0.011	0.22	....	....	0.002	0.010	Electric
C13	0.77	0.32	0.24	0.017	0.013	....	....	....	0.010	0.010	Electric
B8	0.38	0.47	0.18	0.018	0.022	....	....	....	0.004	0.003	Open-Hearth
Y	0.38	0.78	0.15	0.009	0.020	....	0.38	0.085	0.005	0.010	Induction
A	0.17	0.51	0.06	0.020	0.029	....	....	....	0.004	0.010	Open-Hearth
X	0.17	0.54	0.21	0.009	0.018	....	0.54	....	0.006	0.020	Induction
S	0.37	0.70	0.16	0.019	0.020	0.18	....	....	0.002	0.020	Unknown
B6	0.39	0.70	0.20	0.015	0.022	....	....	....	0.006	0.003	Open-Hearth
B10	0.28	0.83	0.13	0.019	0.023	....	....	....	0.009	0.004	Unknown

Table II
Deoxidation Practice and Grain Growth Characteristics of Steels

Number	Deoxidation Practice	A.S.T.M. Austenite Grain Size of Case 8 Hours at Carburizing Temperature — Degrees Fahr. 1600	1700	1800	1900
C11	Al 3 lbs. per ton	4–5	4–5	4–5	.
C13	(a)	6–8	4–5	4–5	.
B8	Al 0.75 lbs. per ton	6	6	3	1
Y	..	.	4	.	.
A	(a)	4	3	3	2
X	..	.	3	.	.
S	..	8	8	7 & 2	4 & 2
B6	Al 1 lb. per ton	7	5–6	4	–2–
B10	(a)	6	6	2 & 6	1

(a) Aluminum added as 5 oz. in top 6 inches of ingot.

All of these steels have been subjected to at least one grain growth test and most of them have been tested over the range of 1600 and 1900 degrees Fahr. (870 and 1040 degrees Cent.). Table II shows the deoxidation practice insofar as data could be obtained and shows the grain sizes developed in the case on carburizing eight hours at the various temperatures. These steels would be rated as fine, medium and coarse-grained by the McQuaid-Ehn test.

These commercial steels were given a 114- to 150-hour subcritical spheroidizing treatment to produce structures suitable for carbide solution study.

From these steels thus treated, specimens $\frac{3}{8}$ inch square by $\frac{3}{32}$ inch in thickness were prepared and given solution treatments at temperatures ranging from 1400 to 1700 degrees Fahr. (760 to 925 degrees Cent.) and for time intervals ranging from 1 second to 30 minutes at temperature. The specimens were immersed in a lead bath for the desired time interval at the desired temperature for heating, followed by an immediate quench in either water or a 2.5 per cent NaOH solution.

With the aid of a thermocouple inserted in the center of a dummy specimen it was found that approximately 2 seconds was required to bring the small specimen up to the temperature of the bath. Therefore the time at temperature reported in the data is 2 seconds less than the total time in the bath and is believed to be accurate to the closest second.

Quenching of the specimens was accomplished by a speedy withdrawal of the specimen from the lead bath, followed by an immediate quench into still water or NaOH solution at room temperature. The specimens were simply immersed in the quenching medium, no

stirring action being imparted to them. Since the volume of the specimen was so small compared to the volume of the quenching medium, the specimen was brought to the temperature of the bath very quickly. The specimens (2 or 5 in a group) were treated simultaneously by means of a special holder in order to eliminate any variables in technique. The temperature of the lead bath was maintained by a controller to within ± 5 degrees Fahr. of the desired temperature.

Handling of the small specimens in the lead bath and quenching medium was accomplished by means of a 6-inch length of $\frac{1}{16}$-inch welding rod spot welded to a corner of each specimen. In this manner little heat transfer took place through the handling device. Care was exercised in making hardness determinations and microscopic examination to avoid using the corner of the specimen affected by the heat imparted during the spot welding operation.

Following the solution treatment, from 7 to 10 Rockwell "C" hardness values were determined on a polished face of each specimen. The specimens were then prepared for microscopic examination. Certain of the specimens were tempered for 45 minutes at 700 degrees Fahr. (370 degrees Cent.) to bring out the desired contrast in the microstructure.

Spheroidized Carbide Structures

In order to produce structures consisting of coarse carbide particles in a ferrite matrix as shown in Figs. 1 to 8 inclusive, the steels used in the present investigation were given long subcritical holding treatments, 114 to 150 hours. The photomicrographs show that there is a wide variation in the size and distribution of the carbide particles in the different steels from essentially the same spheroidizing treatments.

The steels shown in Figs. 1 and 2 have essentially the same chemical composition except that "C11" (Fig. 1) contains 0.22 per cent vanadium which apparently is effective in causing coalescence of the carbide particles into massive carbides. Steel "C13", however, had a higher nitrogen content, 0.010 per cent as compared with 0.002 per cent in "C11", and it may well be that the nitrogen content was an important factor in controlling carbide growth.

Steels "B8" and "Y", Figs. 3 and 4, show closely related analyses except that steel "Y" contains 0.38 per cent molybdenum and 0.085 per cent chromium. The effect of this alloy addition

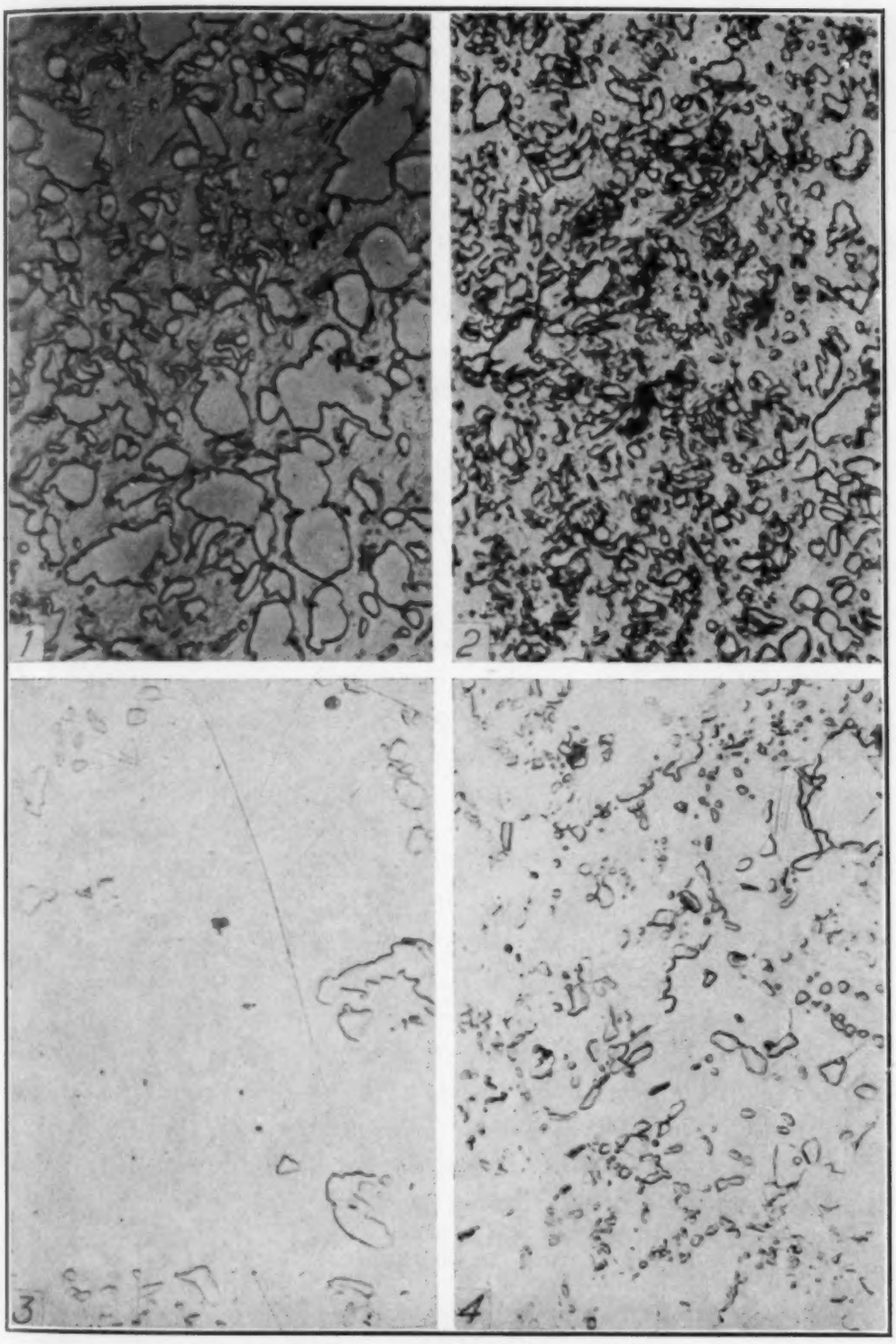


Fig. 1—C11 Held 114 Hours at 1300-1325 Degrees Fahr. × 1000.
Fig. 2—C13 Held 114 Hours at 1300-1325 Degrees Fahr. × 1000.
Fig. 3—B8 Held 114 Hours at 1300-1325 Degrees Fahr. × 1000.
Fig. 4—Steel Y Held 150 Hours at 1325 Degrees Fahr. × 1000.

appears to be to prevent coalescence of the carbide particles resulting in a more uniform size and distribution of the carbide particles. The nitrogen contents of these two steels are essentially the same, but steel "Y" is materially higher in total aluminum content.

The structures of the two low carbon steels "A" and "X" are shown in Figs. 5 and 6. Steel "A" and "X" have essentially the same analyses except that "X" contains 0.54 per cent molybdenum. These steels were given identical spheroidizing treatments and it is interesting to observe the marked effect of the 0.54 per cent molybdenum in preventing the growth of the carbide particles. Attention should be called to the fact that the plain carbon steel "A" shows widely separated, rather coarse carbide particles as compared to the more uniform structures of the alloy steel "X". The nitrogen contents of these two steels are essentially the same, but steel "X" contains twice as much total aluminum. This marked difference in carbide distribution is reflected in the hardening characteristics, as will be discussed later.

Figs. 7 and 8 show the difference in structures of steel "B6" and "S". The vanadium-containing steel shows finer carbides and if this is attributed to vanadium, the effect of the vanadium in this case is just the opposite to its effect in steel "C11" (Fig. 1) as compared with steel "C13" in Fig. 2. However, it should be noted that steel "S" contains 0.02 per cent total aluminum as compared with 0.003 per cent in steel "B6".

Steel "B10" happened to be heated high enough in the spheroidizing treatment that on cooling it contained areas of pearlite and some undissolved carbides in a ferrite matrix as shown in Fig. 9. Thus this steel is not available for comparison of the size and distribution of the carbides after the long subcritical temperature treatment. It has been used in the test to be discussed later under Rockwell "C" hardness studies. Presumably the slightly higher manganese content (0.83 per cent) of steel "B10" lowered its lower critical temperature enough that this steel was heated into the critical range while the others were not.

While it is not fundamental to the present study, it is of interest to draw conclusions regarding those factors which favored or hindered the formation of large carbide particles in the long heatings at slightly subcritical temperatures.

Comparing steels "C11" and "C13" (Figs. 1 and 2) it must be concluded that 0.22 per cent vanadium favors carbide growth or that

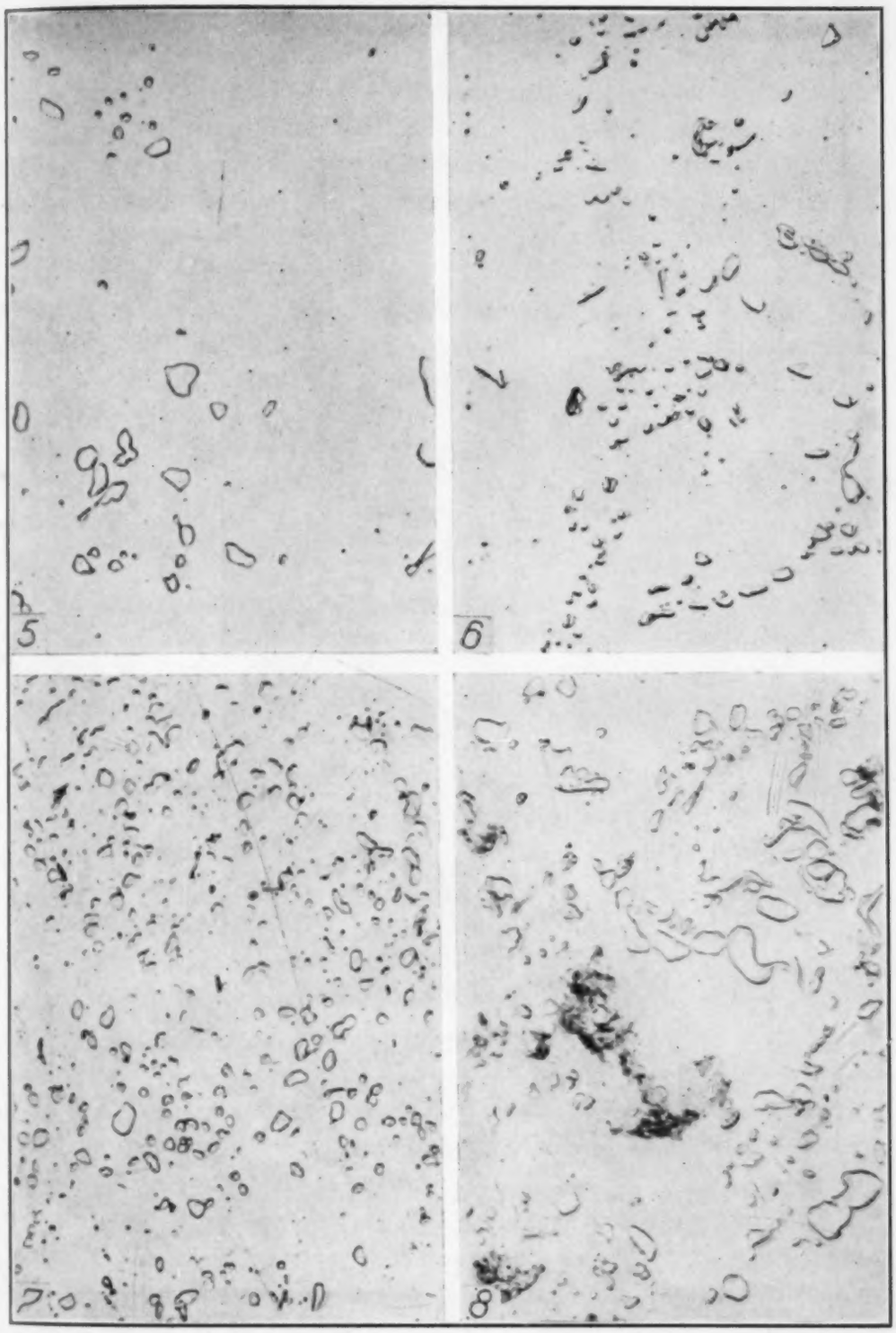


Fig. 5—Steel A Held 150 Hours at 1325 Degrees Fahr. × 1000.
Fig. 6—Steel X Held 150 Hours at 1325 Degrees Fahr. × 1000.
Fig. 7—Steel S Held 150 Hours at 1325 Degrees Fahr. × 1000.
Fig. 8—B6 Held 114 Hours at 1300-1325 Degrees Fahr. × 1000.

the 0.010 per cent nitrogen in steel "C13" as contrasted with only 0.002 per cent nitrogen in steel "C11" is the more important factor. Aluminum or alumina do not seem to be involved.

Comparing steels "B8" and "Y" (Figs. 3 and 4) the factors which may be selected as possible inhibitors are molybdenum (0.38 per cent), chromium (0.085 per cent) and total aluminum (0.010 per cent).

Comparing steels "A" and "X" the two factors which seem most likely to have inhibited carbide growth are molybdenum (0.54



Fig. 9—B10 Held 114 Hours at 1300-1325 Degrees Fahr. × 1000.

per cent) and total aluminum (0.020 per cent) in steel "X" while steel "A" contained no molybdenum and only 0.010 per cent total aluminum.

Comparing steels "S" and "B6" the vanadium (0.18 per cent) and aluminum (0.020 per cent vs. 0.003 per cent in steel "B6") are selected as probable factors. Since vanadium was either a promoter of carbide coarsening in steel "C11" as compared with "C13" or was dominated by the nitrogen (0.010 per cent) it seems reasonable to conclude that the relatively high aluminum (probably nearly all as Al_2O_3) is the more important factor. There are two other com-

parisons in which the aluminum could have been an important factor in controlling carbide growth but in each case molybdenum was present and in one case chromium was also present in the material which showed the finer carbides.

From the very limited number of compositions of steels studied it is suggested that nitrogen and total aluminum (probably Al_2O_3) are important factors in inhibiting the growth of carbide particles in hypoeutectoid steels upon long heating at temperatures just below the lower critical. These factors may be more important in these steels than the presence of some atoms of vanadium or molybdenum or chromium in the ferrite lattice. With higher alloy contents and the presence of different carbides the situation may be changed, however.

It should be evident from the photomicrographs just discussed that the type of structures used in this investigation is definitely more unfavorable for carbide solution and the formation of austenite than are ordinary commercial structures.

Grossmann (6) has demonstrated that austenite grains form at the cementite-ferrite interfaces of pearlite areas. Attention should be called to the great difference in the cementite-ferrite interfacial area of a structure such as is shown in Fig. 5 as compared to an ordinary commercial pearlitic or finely spheroidized cementite structure.

To enable the complete formation of austenite in a structure such as is shown in Fig. 5, solution of the carbides must first take place by reaction of the ferrite at the surface of the comparatively few, large carbide particles, followed by assimilation of the large surrounding ferrite areas by the carbon-rich austenite surrounding each large carbide particle. As diffusion of the carbon in the carbon-rich austenite takes place through the surrounding ferrite, more carbon is continually fed to the austenite surrounding each carbide particle until the original carbides are completely dissolved. It then remains for a further diffusion of the carbon to take place until a uniform carbon content of the austenite results. In the case of a pearlitic structure consisting of alternate plates of ferrite and carbide there is a much greater ferrite-cementite interfacial area for solution and diffusion from which it would be expected that complete carbide solution and formation of a uniform carbon content austenite would occur considerably faster than it would in the structures used in the present investigation.

Hardness Determinations

The average Rockwell "C" hardness value was determined, after quenching, for each specimen given a solution treatment. Figs. 10 to 13 show these values plotted as a function of time at temperature prior to the quench. It will be noted from a study of the photomicrographs to be discussed later representing structures developed at various points on the hardness curves, that the hardness observed is closely related to the amount of carbide solution that took place prior to the quench. In other words, the hardness that can be developed is believed to be dependent upon the amount of carbon actually in solution at the instant of quenching, but that this relation is limited in its application to perhaps 0.50 to 0.60 per cent dissolved carbon.

All steels, unless specified otherwise in the data, had slightly less than zero Rockwell "C" hardness as a result of the spheroidizing treatment. Accordingly, any measurable hardness on the Rockwell "C" scale could result only from a solution of the carbides and diffusion of carbon in the austenite. Therefore, the curves of Figs. 10 to 13 give a rather complete picture of the rate of carbide solution in the various steels at the various temperatures investigated. Table III gives a sample of the individual Rockwell "C" hardness values used in determining the average hardness. Other hardness data are not tabulated because the results are shown in curves.

Table III
Rockwell "C" Values for Specimens of Steel "Y" Held at 1500 Degrees Fahr.

Value No.	Time at Temperature in Seconds								
	5	15	30	60	120	360	480	900	1800
1	36.2	46.5	52.4	55.5	54.0	59.0	59.6	59.0	58.8
2	34.8	48.1	52.2	57.0	54.0	57.8	57.1	56.0	57.0
3	38.0	50.1	52.3	57.5	56.0	58.2	57.0	58.8	56.0
4	40.0	49.5	52.2	58.0	52.2	58.1	57.0	57.2	55.0
5	37.5	49.6	51.9	56.0	52.3	57.1	59.0	56.2	53.0
6	37.0	50.0	53.4	56.5	52.3	57.6	59.6	59.2	56.5
7	35.4	49.1	52.1	54.6	52.3	58.0	59.2	56.8	58.8
8	34.0	49.6	52.1	56.0	53.4	57.0	59.8	59.0	58.2
9	35.1	51.2	52.5	57.0	58.0	59.0	59.6	59.2	59.0
10	35.6	49.2	52.8	57.8	59.0	58.6	58.2	58.5	58.3
Aver.	35.4	49.3	52.4	56.6	54.8	58.0	58.6	57.9	57.1

Fig. 10 shows the relation of hardness of quenched specimens of the low carbon steels "A" and "X" to holding time at various temperatures. Figs. 11 and 12 show similar relations for the medium-

carbon steels, while the curves for the higher carbon (hypoeutectoid) steels are shown in Fig. 13.

In the case of steels C11 and C13, as shown later in the photomicrographs, it appears that in steels of this carbon content (0.78 and 0.77 per cent), only partial solution of the carbides is necessary for the development of maximum hardness upon quenching. This

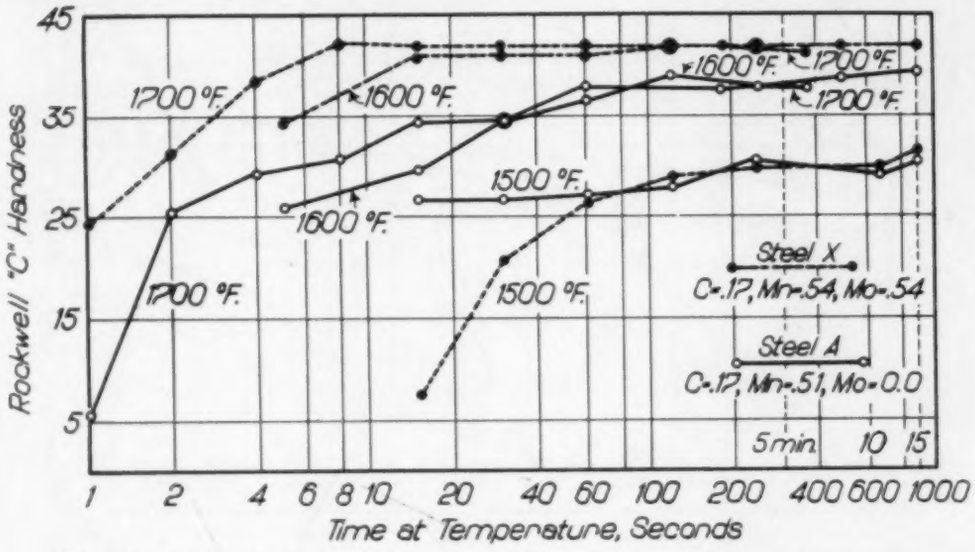


Fig. 10—Effect of Holding Time and Temperature on Rockwell "C" Hardness of Low Carbon Steels "A" and "X." Specimens Quenched in Water at 80 Degrees Fahr.

is in agreement with the findings of Burns, Moore, and Archer (8) who found that an increase in carbon content beyond the neighborhood of 0.55 per cent carbon had no effect upon increasing the hardness that could be obtained upon quenching. In view of their findings and also of the present data, it is believed that as soon as this critical amount of carbon is in solution (necessitating as it would only partial carbide solution), maximum hardness may be developed and it is suggested that there is then a decreased tendency for further carbide solution. Thus it is believed that the hardness curves for steel C11 and C13 indicate the rapid rate of solution of this critical amount of carbon. It was indeed interesting to find that in steel "C13", solution of this critical amount of carbon occurred within just 1 second at a holding temperature of 1600 degrees Fahr. (870 degrees Cent.).

The rest of the steels studied contained considerably less than the critical amount of carbon and it is apparent from a study of the photomicrographs representing maximum hardness points on the curves that complete carbide solution must occur before maximum hardness can be developed. Accordingly, the curves for these steels

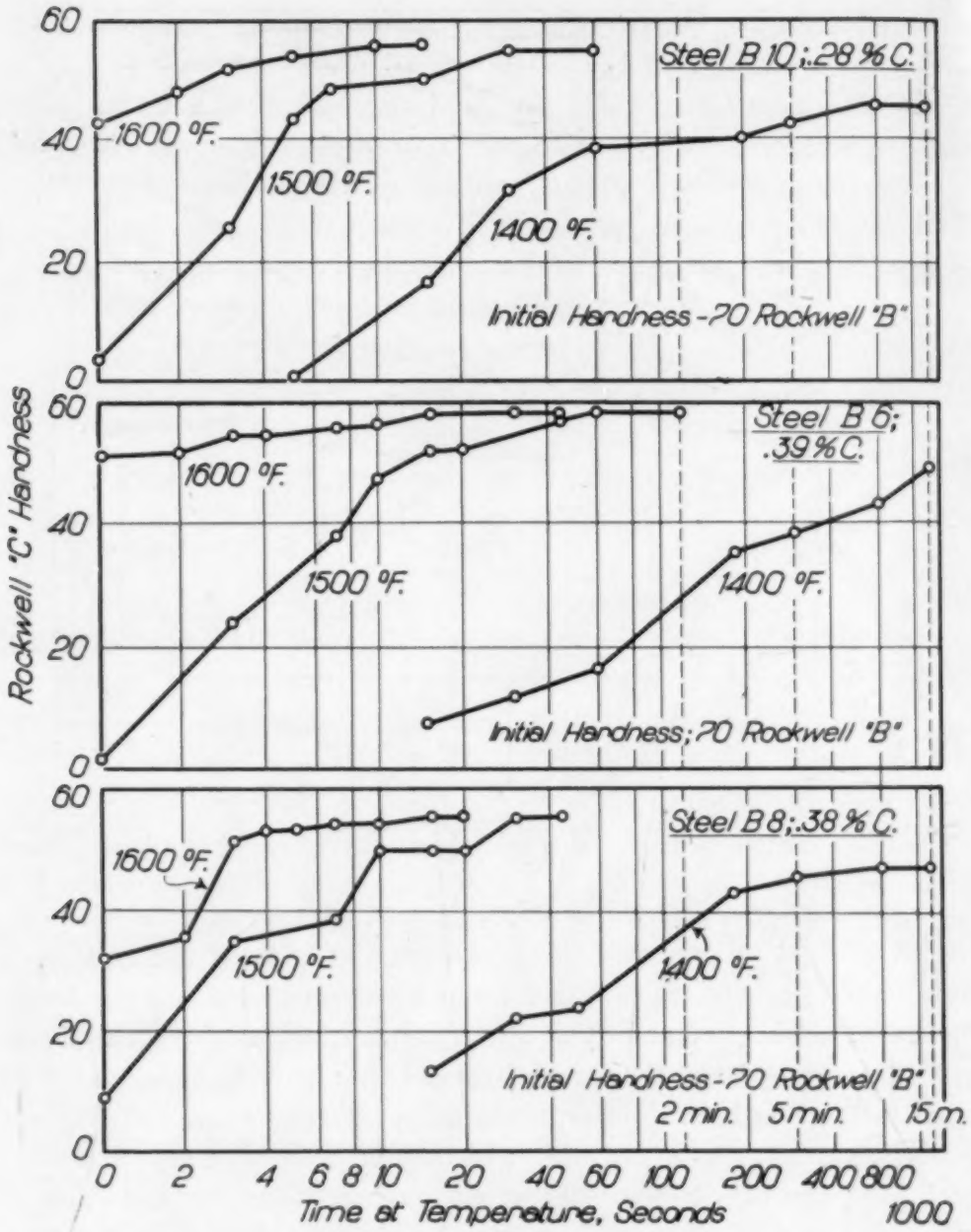


Fig. 11—Effect of Holding Time and Temperature on Rockwell "C" Hardness of Medium Carbon Steel "B6," "B8" and "B10." Specimens Quenched 2.5 Per Cent NaOH Solution.

indicate rather accurately the rate of carbide solution and it is to be noted that complete carbide solution (indicated by maximum hardness points on the curves) occurs in a surprisingly short time at the temperatures studied. Maximum hardness was not developed at temperatures between the lower and upper critical (Ac_1 and Ac_3) even though complete carbide solution had occurred because of the

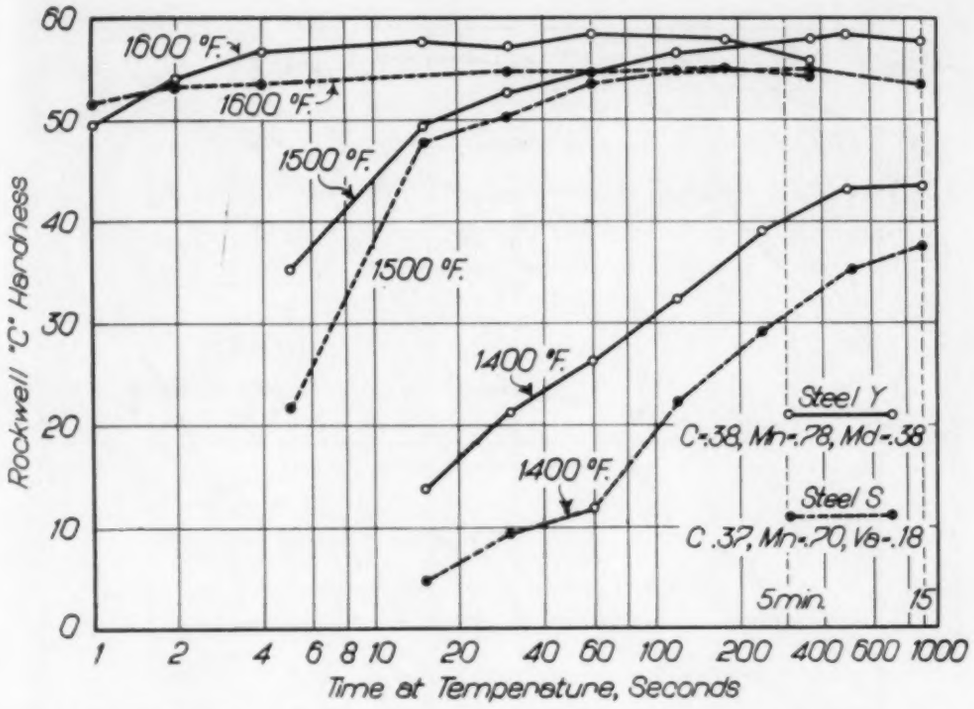


Fig. 12—Effect of Holding Time and Temperature on Rockwell "C" Hardness of Medium Carbon Steels "S" and "Y." Specimens Quenched in 2.5 Per Cent NaOH Solution.

undissolved ferrite remaining in equilibrium in this temperature range.

Attention should be called to the effect of 0.54 per cent molybdenum in steel "X" (Fig. 10) as compared with the plain carbon steel "A". It appears to increase the rate of carbide solution and maximum hardness attainable upon quenching. This difference may be partly accounted for by the marked difference in the size and distribution of the carbides in the original structures.

Study of Microstructures

Microscopic examination of specimens quenched from several temperatures after various holding times was the principal means of studying the rate of carbide solution in the present investigation. This method of study also made it possible to determine the amount of undissolved ferrite, which was important in certain specimens, especially when they were heated at temperatures below their upper critical. More than 100 photomicrographs have been prepared and many other specimens have been examined. Only selected microstructures are presented in this paper.

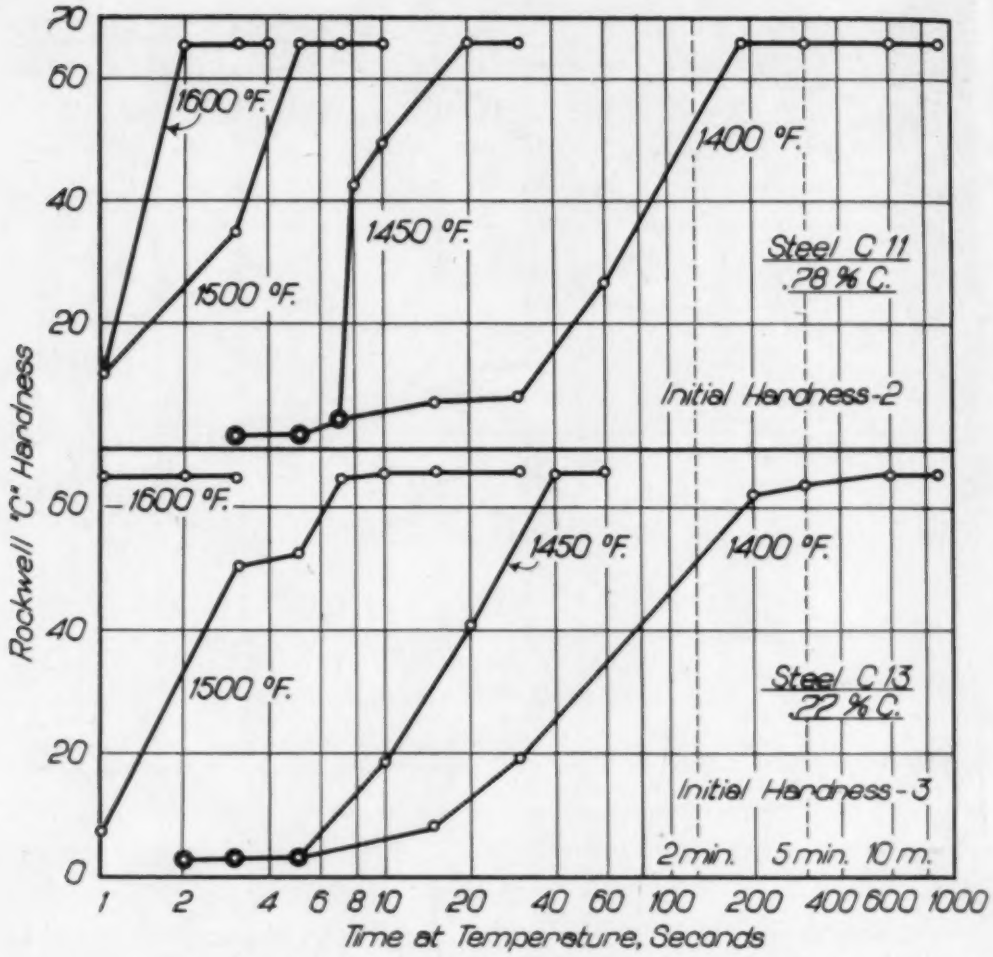


Fig. 13—Effect of Holding Time and Temperature on Rockwell "C" Hardness of Higher Carbon Steels C11 and C13. Specimens Quenched in 2.5 Per Cent NaOH Solution.

After trying various methods of etching it was found desirable to temper all quenched specimens at 700 degrees Fahr. for 45 minutes. The etchant used on the tempered specimens was Vilella's reagent. This metallographic procedure brought out the desired contrast in microstructure showing the undissolved carbides as smooth white particles generally in relief, the ferrite as rough white areas (in some cases the ferrite was polished nearly as smoothly as the carbides), and the austenite (changed to martensite by the quench and tempered to troostite or sorbite) as a dark constituent, the degree of darkening depending somewhat on the carbon concentration of the austenite before the quench. Thus the carbide solution was readily followed by observing the decrease in carbide particle size, decrease in size and number of ferritic areas, and increase in size and number of austenitic areas. After the carbides were dissolved, the progress

of carbon diffusion was observed by the manner of etching of the austenite (troostite or sorbite in the photomicrographs) i.e., areas rich in carbon prior to the quench showed more darkening by the etchant than did areas having a lower carbon concentration. Thus a rough idea as to the difference in carbon content throughout the austenite could be gained.

Microstructures of Low Carbon Steels—Steels "A" and "X" each have 0.17 per cent carbon and may be taken as representative of this type of steel. Their structures after spheroidization are shown in Figs. 5 and 6 and it will be noted that steel "A" had coarser carbide particles. The hardness curves for these steels are shown in Fig. 10.

Since the commercial heat treating temperature for a steel of this analysis would be about 1700 degrees Fahr. (925 degrees Cent.) the photomicrographs to show the carbide solution have been selected from tests made at that temperature. Figs. 14 and 15 show the structure of steels "A" and "X" respectively after 2 seconds at 1700 degrees Fahr. The larger carbide particles in steel "A" (Fig. 14) have not completely dissolved and the austenite area is much less extensive than in steel "X" in Fig. 15. It appears that the finer carbides in steel "X" have completely dissolved in 2 seconds at 1700 degrees Fahr. (925 degrees Cent.). In spite of the larger amount of ferrite in steel "A" the hardnesses of the quenched specimens are essentially the same.

The microstructures of steels "A" and "X" after holding 8 seconds at 1700 degrees Fahr. (925 degrees Cent.) are shown in Figs. 16 and 17 respectively. The carbides have completely dissolved and excess ferrite is no longer evident. The hardnesses were 30.8 and 42.2 Rockwell "C" for steels "A" and "X" respectively. This was the maximum for steel "X" but steel "A" showed a further increase in hardness on longer heating to a maximum of about 37. It is thought that the slower development of full hardness of steel "A" is due to the longer time required for uniform diffusion of the carbon in the austenite. Steel "X" developed a higher hardness which apparently can be attributed to its molybdenum content.

At 1600 degrees Fahr. (870 degrees Cent.) steel "A" developed essentially the same hardness as at 1700 degrees Fahr. (925 degrees Cent.) after about 30 seconds while steel "X" showed full hardness after 15 seconds. At 1500 degrees Fahr. (815 degrees Cent.) neither of these steels developed full hardness even in 900 seconds. At this

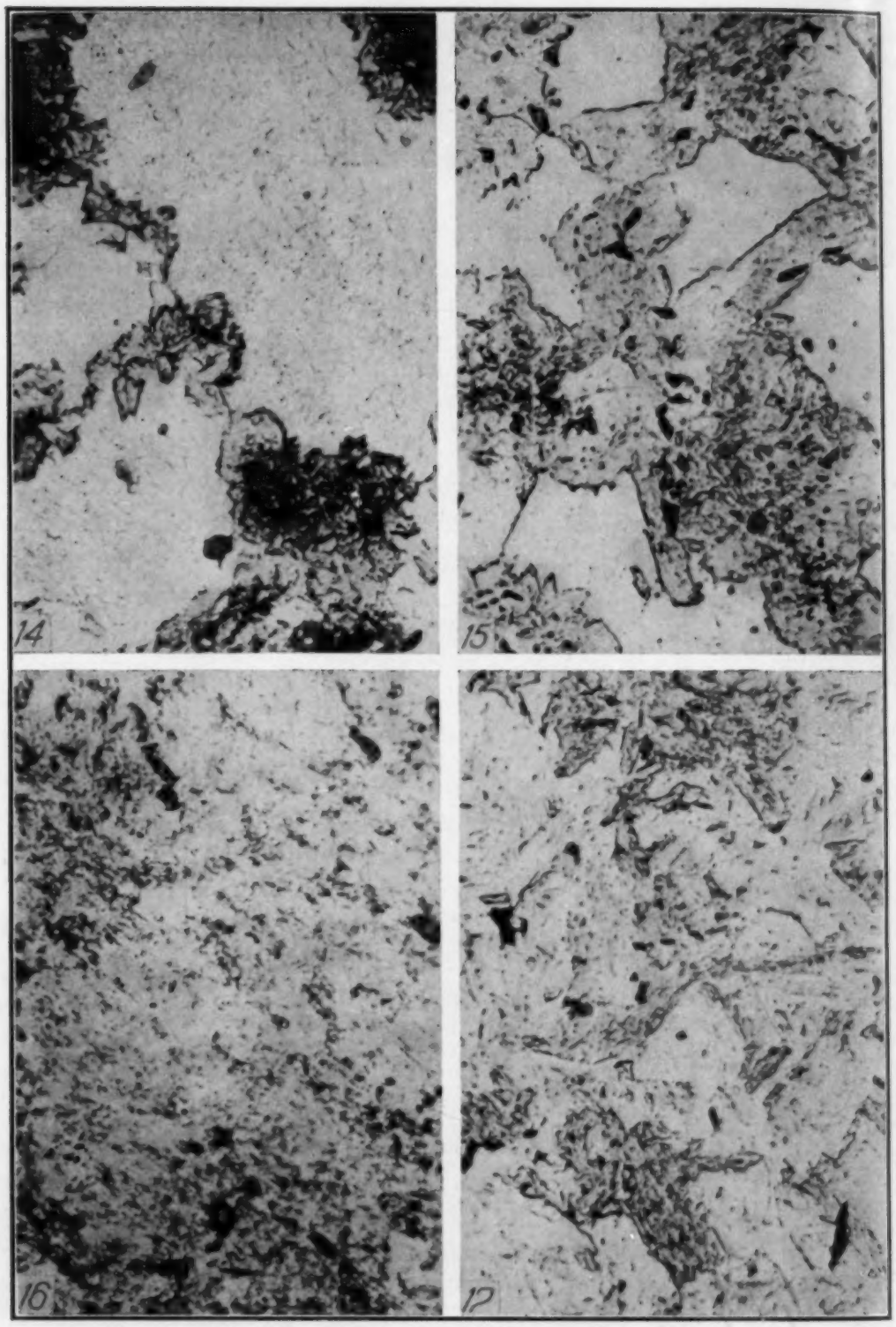


Fig. 14—Steel "A" Held 2 Seconds at 1700 Degrees Fahr. Aver. Rockwell "C" 25.5.
Fig. 15—Steel "X" Held 2 Seconds at 1700 Degrees Fahr. Aver. Rockwell "C" 24.7.
Fig. 16—Steel "A" Held 8 Seconds at 1700 Degrees Fahr. Aver. Rockwell "C" 30.8.
Fig. 17—Steel "X" Held 8 Seconds at 1700 Degrees Fahr. Aver. Rockwell "C" 42.2.
All Photomicrographs × 1000

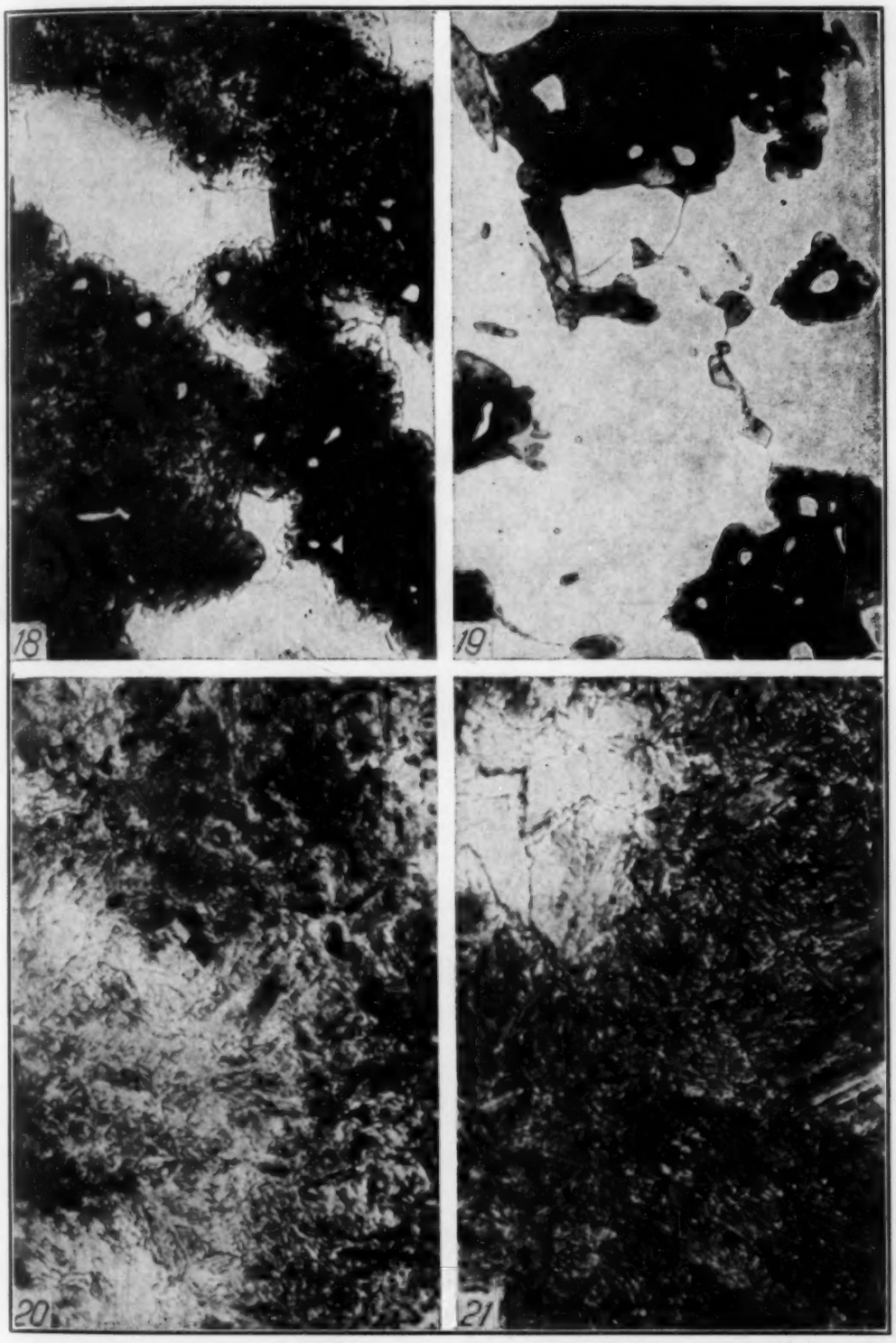


Fig. 18—Steel "B6" Held 1 Second at 1600 Degrees Fahr. × 1000.
Fig. 19—Steel "B8" Held 1 Second at 1600 Degrees Fahr. × 1000.
Fig. 20—Steel "B6" Held 15 Seconds at 1600 Degrees Fahr. × 1000.
Fig. 21—Steel "B8" Held 15 Seconds at 1600 Degrees Fahr. × 1000.

temperature free ferrite was always present but the carbides were practically all in solution after 4 minutes.

Microstructures of Medium Carbon Steels—Steels "B8", "Y", "S", "B6" and "B10" are in the medium carbon group. Steel "Y" contains 0.38 per cent molybdenum and 0.085 per cent chromium while steel "S" contains 0.18 per cent vanadium. Steels "B6" and "B8" may be taken as representative of this group without alloying elements.

The spheroidized structures of steels "B6" and "B8" are shown in Figs. 8 and 3 respectively. "B8" shows larger areas containing no carbides. The hardness data for these steels are shown in Figs. 11 and 12.

The microstructures of steels "B6" and "B8" after heating 1 second at 1600 degrees Fahr. (870 degrees Cent.) are shown in Figs. 18 and 19 respectively. These micrographs furnish a good illustration of the effect of carbide distribution and size on the rate of formation of austenite; the larger ferrite areas in steel "B8" as spheroidized are still evident after 1 second at 1600 degrees Fahr. (870 degrees Cent.). The quenched hardness is in good agreement with the microstructures. From the hardness curves in Fig. 11 it is indicated that steel "B6" develops full hardness in about 15 seconds while steel "B8" does not develop as high hardness and its hardness is continuing to increase slightly at this holding time. The microstructures of steels "B6" and "B8" after heating 15 seconds at 1600 degrees Fahr. (870 degrees Cent.) are shown in Figs. 20 and 21 respectively. Both show complete disappearance of the carbides, but steel "B6" shows areas in which low carbon content is indicated and steel "B8" actually shows a small amount of undissolved ferrite.

At 1500 degrees Fahr. (815 degrees Cent.) the holding times to effect full hardness for steels "B6" and "B8" were about 45 to 30 seconds respectively. However, the ferrite in "B8" required between 120 and 300 seconds for complete solution. Similar data for "B6" were not obtained.

Steels "S" and "Y" of the medium carbon group are of interest because of their slight alloy contents. Their structures after the spheroidizing treatments are shown in Figs. 7 and 4 and their hardness curves in Fig. 12.

The structures of steels "S" and "Y" after 1 second at 1600 degrees Fahr. (870 degrees Cent.) are shown in Figs. 22 and 23 respectively. There has been considerable solution of carbides but

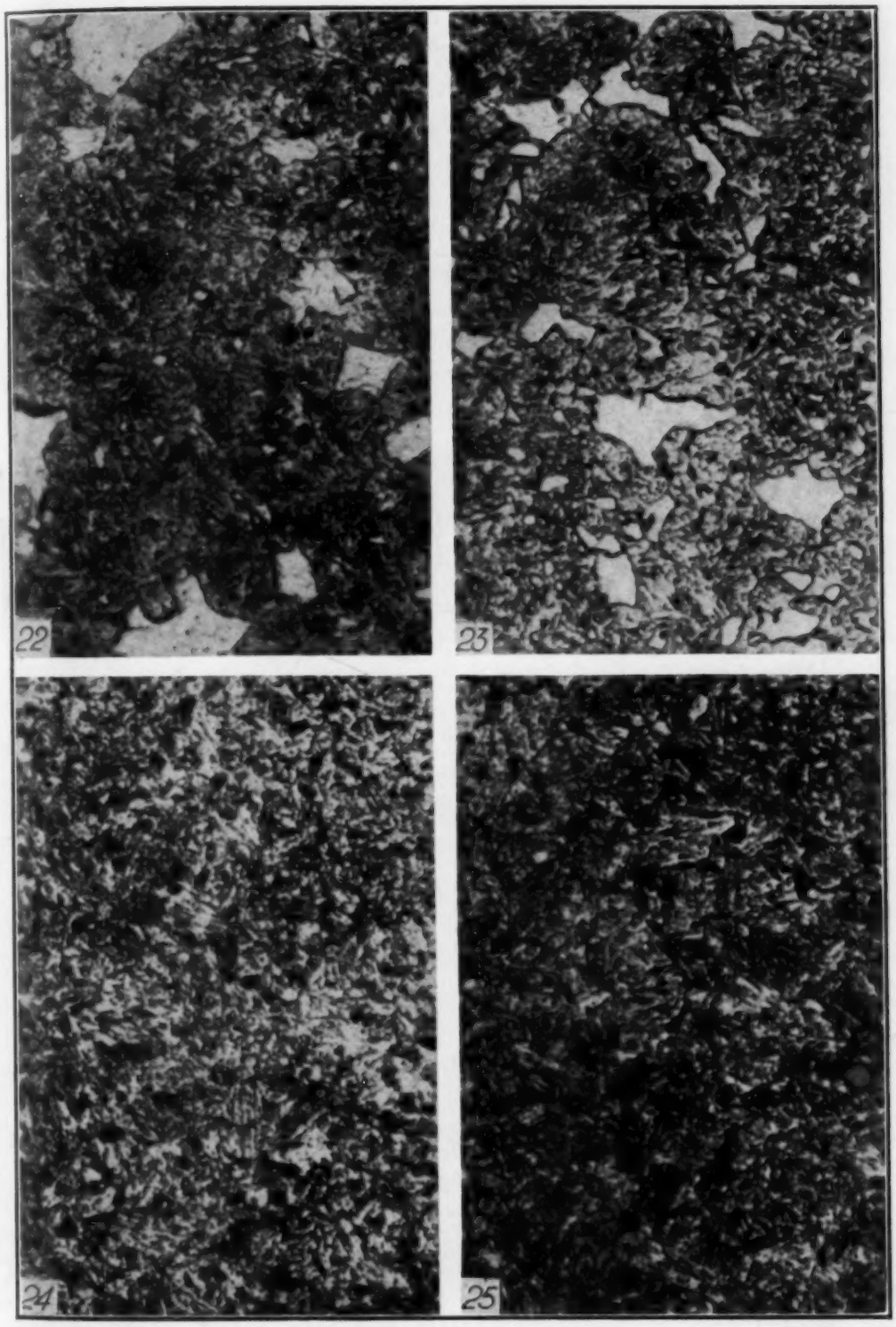


Fig. 22—Steel "S" Held 1 Second at 1600 Degrees Fahr. Aver. Rockwell "C" 51.7.
Fig. 23—Steel "Y" Held 1 Second at 1600 Degrees Fahr. Aver. Rockwell "C" 49.7.
Fig. 24—Steel "S" Held 4 Seconds at 1600 Degrees Fahr. Aver. Rockwell "C" 53.5.
Fig. 25—Steel "Y" Held 4 Seconds at 1600 Degrees Fahr. Aver. Rockwell "C" 56.8.
All Photomicrographs × 1000

this reaction is not complete and excess ferrite is evident. It is of special interest to note that after only 1 second at 1600 degrees Fahr. (870 degrees Cent.) and before either the carbides or ferrite have disappeared, steels "S" and "Y" developed Rockwell "C" hardnesses of 52 and 50 respectively.

The structures of steels "S" and "Y" after 4 seconds at 1600 degrees Fahr. (870 degrees Cent.) are shown in Figs. 24 and 25 respectively and the hardness as shown in Fig. 12 are as high as can be developed even after 900 seconds at temperature.

It is of interest to compare the rates of carbide solution of these two low alloy steels with steels "B6" and "B8". The data herein presented show that steel "S" with 0.18 per cent vanadium and steel "Y" with 0.38 per cent molybdenum and 0.085 per cent chromium have a more rapid rate of carbide solution and develop full hardness in a shorter time than steels "B6" and "B8". This relation is probably due in the most part to the somewhat coarser carbide particles in "B6" and "B8" and especially to the larger ferrite areas in "B8" in the spheroidized condition. Certainly there is no indication that the presence of vanadium or molybdenum retards the rate of carbide solution.

Tests on steels "S" and "Y" at 1500 degrees Fahr. (815 degrees Cent.) showed the time required for complete carbide solution was about 120 seconds as compared with 4 seconds at 1600 degrees Fahr. (870 degrees Cent.), thus indicating that the rate of carbide solution is increased about 30 times by increasing the temperature 100 degrees Fahr. Also as shown in Fig. 12 these steels require 60 seconds or more to develop full hardness at 1500 degrees Fahr. (815 degrees Cent.).

At 1400 degrees Fahr. (760 degrees Cent.) neither steel developed full hardness even after 900 seconds at temperature and both showed excess of carbides and ferrite even after 1800 seconds at 1400 degrees Fahr. (760 degrees Cent.). In general, steel "Y" showed a higher hardness than steel "S" and it may be pertinent to note that steel "Y" showed a grain size of 4 in the McQuaid-Ehn test while steel "S" showed a grain size of 8 and contained twice as much total aluminum (probably present as Al_2O_3) as did steel "Y".

Steel "B10" is lower in carbon than the other steels in this group and as shown in Fig. 9 was not spheroidized like the others. For these reasons it is not readily comparable with the others, but the hardness curves for steel "B10" are shown in Fig. 11.

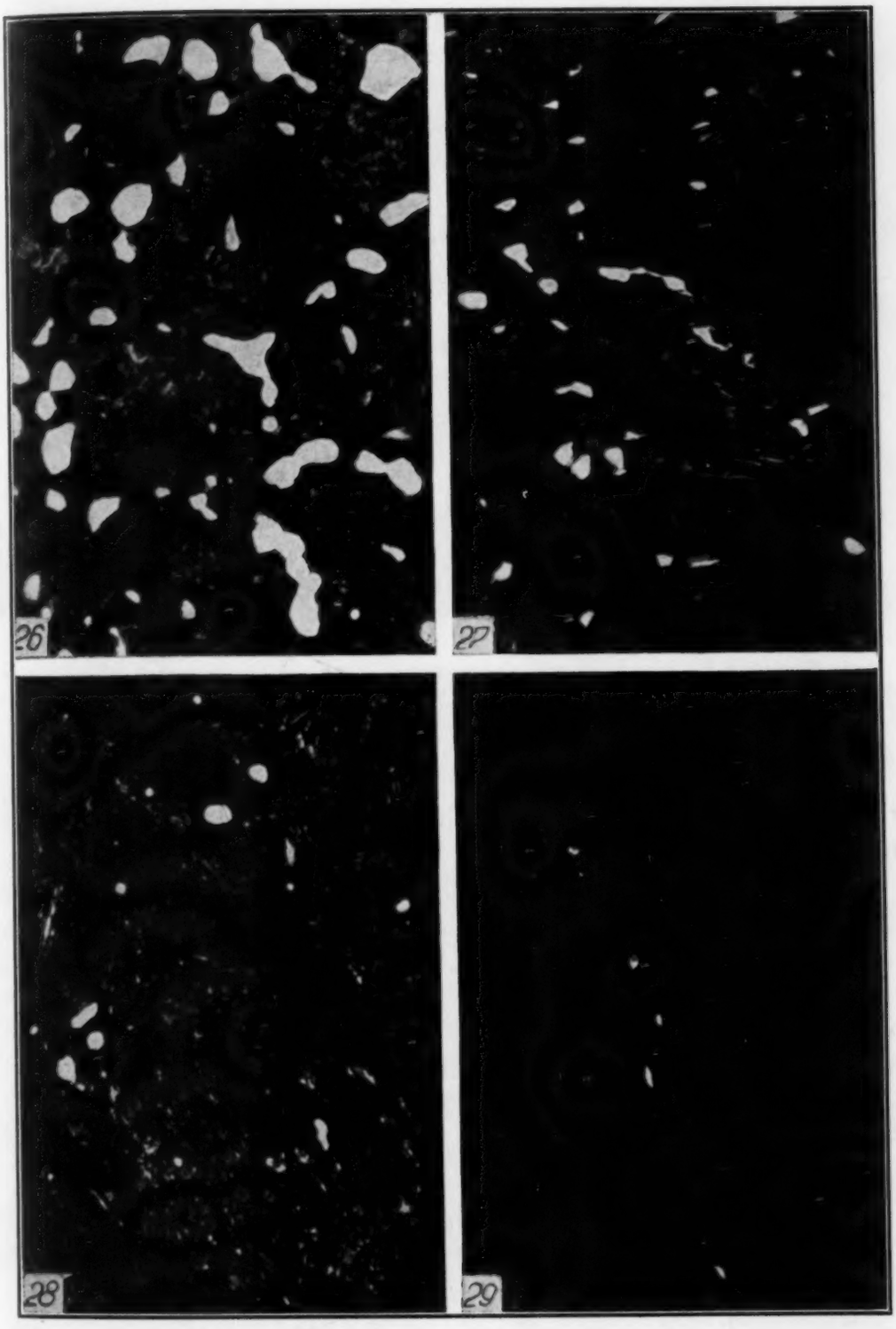


Fig. 26—Steel "C11" Held 2 Seconds at 1600 Degrees Fahr. × 1000.
Fig. 27—Steel "C13" Held 1 Second at 1600 Degrees Fahr. × 1000.
Fig. 28—Steel "C11" Held 600 Seconds at 1600 Degrees Fahr. × 1000.
Fig. 29—Steel "C13" Held 60 Seconds at 1600 Degrees Fahr. × 1000.

Higher Carbon Steels—Steels "C11" and "C13" represent higher carbon materials, but are still hypoeutectoid in composition. These steels are quite close in chemical composition except that "C11" contains 0.22 per cent vanadium and only one-fifth as much nitrogen as "C13". Their spheroidized structures are shown in Figs. 1 and 2 and it will be noted that steel "C11" developed much coarser carbides. The hardness curves for these steels are shown in Fig. 13.

Figs. 26 and 27 show the undissolved carbides in steels "C11" and "C13" after 2 and 1 seconds at 1600 degrees Fahr. respectively, at which time both steels developed full hardness of 67 Rockwell "C". The slower rate of carbide solution and the longer time for steel "C11" to develop full hardness is thought to be attributable to the larger carbides in the spheroidized structure.

Fig. 28 shows the microstructure of steel "C11" after 600 seconds at 1600 degrees Fahr. while Fig. 29 shows the structure of steel "C13" after 60 seconds at the same temperature. It is evident that the carbides in steel "C11" are much slower in going into solution. The reason for this difference is not evident. The larger size of the carbides in the spheroidized specimens could be a factor and a question may be raised regarding the effect of vanadium. Steel "S" which contained 0.18 per cent vanadium did not show that vanadium retarded the solution of the carbides because the carbides went into solution more rapidly than they did in steels "B6" and "B8" which did not contain vanadium.

At 1500 degrees Fahr. (815 degrees Cent.) which would be nearer to commercial hardening temperatures for a steel of this carbon content, steels "C11" and "C13" developed full hardness in 5 and 7 seconds respectively. Yet the microstructures showed that the carbides were not completely dissolved even after 3600 seconds although they had almost disappeared in steel "C13".

At 1400 degrees Fahr. (760 degrees Cent.) both steels showed undissolved carbides after holding 2 hours (7200 seconds) at temperature although steel "C11" developed full hardness in 180 seconds and steel "C13" in 600 seconds. However, the increase in hardness of "C13" after 180 seconds was slight. It will be noted from Table II that steel "C11" showed a coarser grain size on carburizing at 1600 degrees Fahr. but these steels showed the same grain size in the McQuaid-Ehn test.

The data from the tests on steels "C11" and "C13" show that the time at 1600 and 1500 degrees Fahr. (870 and 815 degrees Cent.)

required to effect enough carbide solution to develop full hardness is quite short, 1 to 7 seconds, and at 1400 degrees Fahr. (760 degrees Cent.) only a few minutes are required. On the other hand, the time required for complete solution of the carbides is quite long—1 to 2 hours or even longer at the lower temperatures. Thus the picture of carbide solubility and the possible effect of undissolved carbides on the growth of the austenite grains in these steels is decidedly different than in steels containing about 0.40 per cent or lower carbon.

Summary and Conclusions

The rate of carbide solution and of austenite formation has been studied in a series of hypoeutectoid plain carbon and low alloy steels. As a supplement to the metallographic studies the hardnesses of all quenched specimens have been determined, thus providing curves for the relation of holding time at various temperatures to the hardness developed in quenched specimens. In general, good correlation has been found between the microstructures and the hardnesses.

The following conclusions seem warranted:

(1) In the low carbon steels (0.17 per cent carbon) the carbon goes into solution quite rapidly at temperatures above the upper critical and the carbon all disappears sooner than the ferrite. In these steels not more than 8 seconds at 1700 degrees Fahr. was required for complete solution of coarsely spheroidized carbides.

(2) In the medium carbon steels (0.30 to 0.40 per cent carbon) the relative rate of carbide and ferrite solution depends upon the testing temperature. Within the critical range, it is possible to dissolve all of the carbides and retain free ferrite. At 1600 degrees Fahr. (870 degrees Cent.) neither the carbide nor the ferrite was all in solution in one second, but in 4 to 15 seconds the carbide had disappeared in all steels tested and the ferrite had disappeared in three out of four steels. One steel definitely showed excess ferrite and another showed areas which were evidently low in carbon after 15 seconds at 1600 degrees Fahr. (870 degrees Cent.).

(3) The rapid rate at which the carbides go into solution in the above two groups of steels, even when coarsely spheroidized, and the short time required for the complete solution of the carbides seem to preclude the possibility of carbides in such steel functioning to inhibit coarsening of the austenite grains.

(4) The times required at temperature to develop full hardness

on quenching the small specimens used seem remarkably short. The medium carbon steels developed full hardness after holding at 1600 degrees Fahr. (870 degrees Cent.) not over about 15 seconds and even at 1500 degrees Fahr. (815 degrees Cent.) the time required to develop full hardness ranges from one-half to less than 10 minutes for the steels studied.

(5) In the two higher carbon steels (0.77 and 0.78 per cent carbon) the time required for enough carbon to go into solution to develop full hardness on quenching was quite short, being 1 to 2 seconds at 1600 degrees Fahr. (870 degrees Cent.) and 5 to 7 seconds at 1500 degrees Fahr. (815 degrees Cent.). These holding times left undissolved carbides and decidedly longer times were required for their complete solution. At 1600 degrees Fahr. (870 degrees Cent.) one of these steels (C13) showed nearly complete carbide solution in 1 minute while the other (C11) reached a similar condition in 10 minutes. At 1500 degrees Fahr. (815 degrees Cent.) steel "C11", which developed the coarser carbides in the spheroidizing treatment, showed a considerable amount of undissolved carbides after 1 hour while steel "C13" showed practically complete solution of the carbides in that length of time.

(6) The only correlation which can be made between grain coarsening of these higher carbon hypoeutectoid steels and carbide solution is that the steels tested showed 4 to 5 grain sizes in both case and core after carburizing for 8 hours at 1700 and 1800 degrees Fahr. (925 and 980 degrees Cent.), whereas it is known that the carbides go into solution at 1600 degrees Fahr. (870 degrees Cent.). Were the carbides the effective grain growth inhibitor it would seem reasonable to expect coarsening of the austenite grains as soon as the carbides had been dissolved.

(7) This work suggests that other factors, such as aluminum and nitrogen contents, may be more important in controlling the coarsening of the carbides on long heating at subcritical temperatures than low alloy contents.

(8) It is indicated that size and distribution of carbides are important factors in the behavior of steels during heating for hardening. Large areas of free ferrite increase the time required for the ferrite to disappear. Large carbides go into solution more slowly than smaller ones and this relation is conspicuous in the steels approaching the eutectoid composition.

(9) Certain indications have been found that the rate of car-

bide solution in the higher carbon hypoeutectoid steels is very rapid until enough carbon is in solution to produce full hardness in quenched specimens, but that the rate for further carbide solution is very much lower.

(10) The data which have been obtained indicate that the carbides in hypoeutectoid steels do not play any significant part in inhibiting austenite grain coarsening.

Acknowledgment

The authors are indebted to Battelle Memorial Institute for permission to publish the results of this study. They are also indebted to the following companies for steels used in this investigation:

Climax Molybdenum Company, Columbia Tool Steel Company, Ford Motor Company, Halcomb Steel Company, Republic Steel Corporation, Steel Company of Canada, Vanadium Corporation of America.

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THE WHITE LAYER STRUCTURE IN THE EROSION OF MACHINE GUN BARRELS

By W. H. Snair and W. P. Wood

Abstract

The nature of the white layer formed during the erosion of machine gun barrels has been studied. Two explanations of the nature of this layer have been advanced by others who have studied this effect. One view is that the layer consists of martensite while the other maintains that the layer is the result of a nitriding action. In the present investigation the constitution of the layer has been studied by metallographic means and the use of X-rays. All the evidence thus obtained indicated the presence of nitrides. Finally, it was found that by duplicating the probable temperature conditions in the gun barrel, it was possible to produce a layer apparently identical with the one observed in eroded gun barrels. The conclusion, therefore, seems warranted that this layer consists of nitrides in solution and not martensite.

EROSION of gun barrels has been defined by Wheeler (1)[1] as the enlargement of the bore and obliteration of the rifling from any cause. There are various causes, but this paper will deal only with the erosion caused by the cracking and spalling of the bore surface due to the formation of a hard layer of low ductility.

The process of erosion is of great importance to makers of gun barrels and especially to the Ordnance Department of the Army. This importance is due to the fact that the average life of a machine gun barrel is between 4000 and 5000 rounds. This extremely short life is due mostly to the loss of accuracy caused by the ruinous effects of erosion. Fig. 1 shows how this wearing of the bore increases with the number of rounds fired. The relation is not linear, but is almost parabolic. The importance of erosion becomes more pronounced as the number of rounds fired increases.

The conditions within the bore of the gun tube at the instant of firing are very severe. The theoretical flame temperature is around

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, W. H. Snair is metallurgist, research department, American Can Co., Maywood, Ill., and W. P. Wood is professor of metallurgical engineering, University of Michigan, Ann Arbor, Mich. Manuscript received March 31, 1938.

2800 degrees Cent. (5070 degrees Fahr.), and the gases have a pressure of 51,000 pounds per square inch. The products of combustion of the powder are CO, CO_2, CH_4, N_2, H_2, and H_2O.

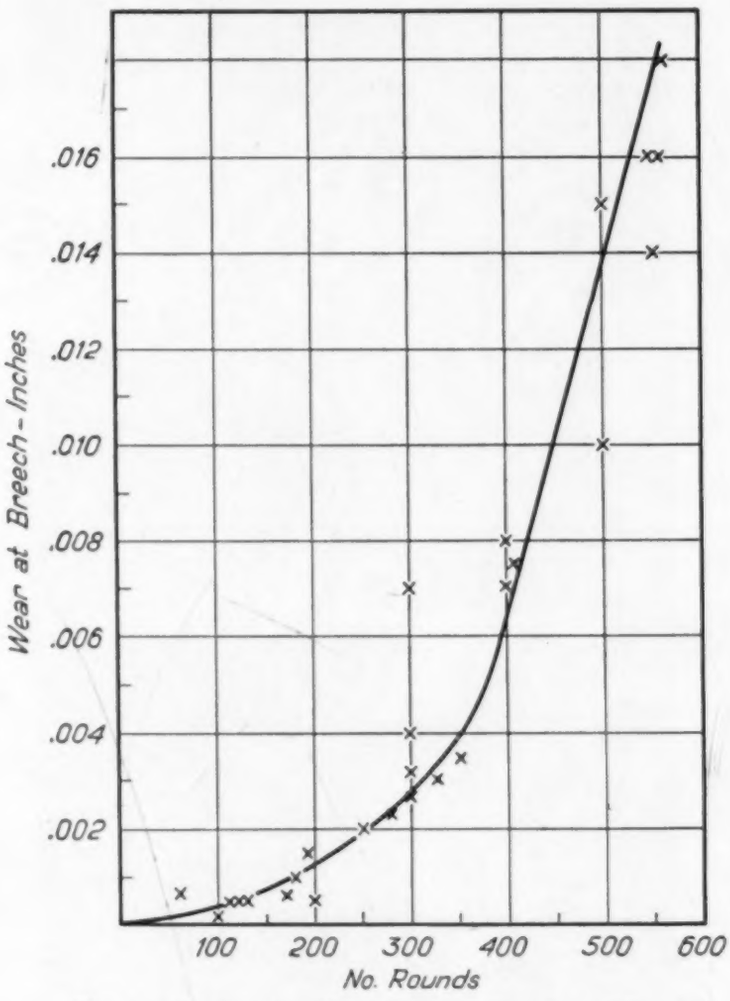


Fig. 1—Erosion in Machine Gun Barrels. Effect of Long Bursts of Fire on the Bore at the Origin of the Rifling.

The layer formed during erosion is glass hard and is very brittle. Under the microscope it appears as a dense white structure incapable of resolution at 1000 diameters. This layer extends for a distance of approximately two and one-half inches along the bore from the origin of the rifling. It varies in depth along this distance, and if the depth were plotted versus the distance along the bore, the resulting curve would closely resemble a powder pressure—distance curve. This fact indicates a definite relationship between the powder pressures developed and the layer formation.

There have been two theories advanced as to the nature of this "white layer," as it is called. The first theory is that the layer is

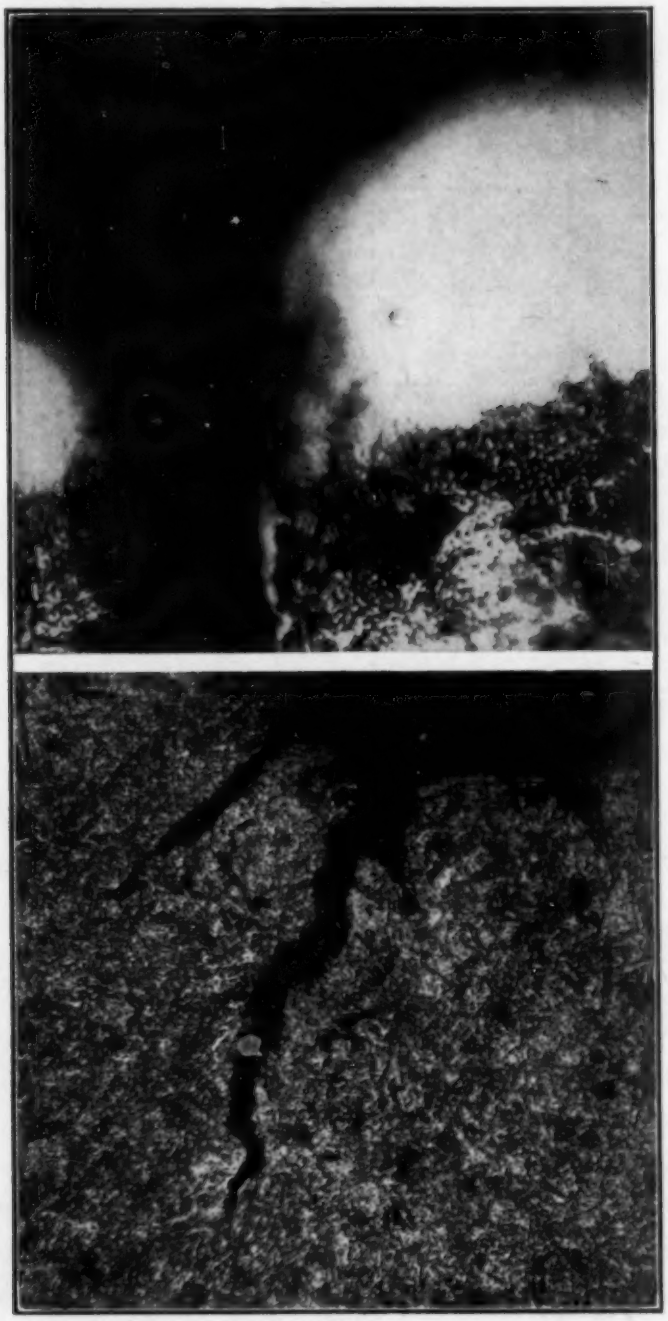


Fig. 2—(Upper) White Layer Structure. × 1000.
Fig. 3—Erosion and Cracking in Bore. × 100.

martensitic in nature and is due to the absorption of carbon at the bore surface. The second theory states that the layer is a solid solu-

tion of nitrides caused by the action of the nascent nitrogen in the exploding gases. It was the purpose of this investigation to attempt

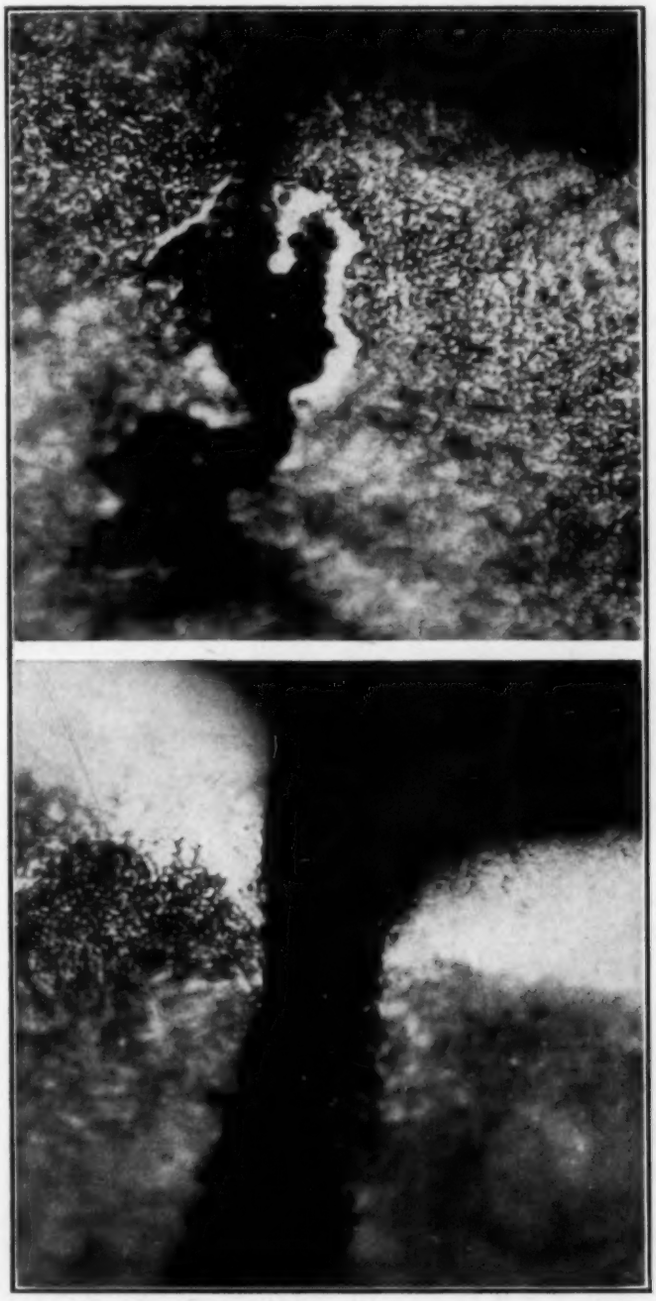


Fig. 4—(Upper) White Layer in a Crack. × 1000.
Fig. 5—(Lower) White Layer After Heating One Hour at 400 Degrees Cent. × 1000.

to determine which was the correct theory in the light of the data presented. It was also the intention to shed some light upon the firing conditions within the gun barrel.

Review of the Literature

Carburization Theory—The carburization theory was advanced by W. W. De Sveshnikoff (2) in 1925. He believed that the white layer was of a martensitic nature, and that it was formed as a result of a rapid quenching of the steel at the bore surface by the large mass of metal surrounding it. De Sveshnikoff believed this was possible because the surface layer absorbed an appreciable amount of carbon from the exploding gases. This gave a carburizing effect to the surface.

De Sveshnikoff stated that when a portion of a gun barrel, containing this layer, was heated to a temperature of 320-390 degrees Cent. (605-735 degrees Fahr.) a darkening of the layer was obtained. This seemed to indicate a troostitic structure for the heated layer. He also claimed to find evidences of martensitic needles in the layer, but no one has ever definitely checked this. An analysis of the filings from the layer showed a varying carbon content with an average of about 37 per cent increase. However, these same filings showed an increase of several hundred per cent for the nitrogen content. De Sveshnikoff did not believe the increase in nitrogen content indicated anything.

Howe (3) believed that in the brief heating period, during the firing, some of the initially distinct particles of ferrite and carbide combined to form austenite. He stated that the austenite cooled rapidly enough to form martensite. He did not believe in the carbon absorption theory.

Dr. Fay (4), in a discussion of De Sveshnikoff's work, stated that he believed the layer was martensite. He, however, attributed the formation to a cold-working effect in the bore. Fay did not believe in the absorption of carbon, for he stated that the rate of erosion was far more rapid than the rate of cementite diffusion and so no more carbon could enter the steel from the exploding gases.

Nitriding Theory—H. E. Wheeler (1) in 1922 stated that he believed the white layer was an austenitic case caused by the alloying effect of nitrogen, which lowered the A_1 point to allow the formation of a nitride solid solution. He compared the layer with the structure found in Haber process cylinders, stating that the two seemed identical.

In 1929, Lester (5) stated that the layer was a solid solution of nitrides. To prove his case, he presented a complete series of photo-

micrographs of the layer. He also heated the layer to temperatures around 400 degrees Cent. (750 degrees Fahr.) and found the layer still persisted. This temperature is above the decomposition tempera-

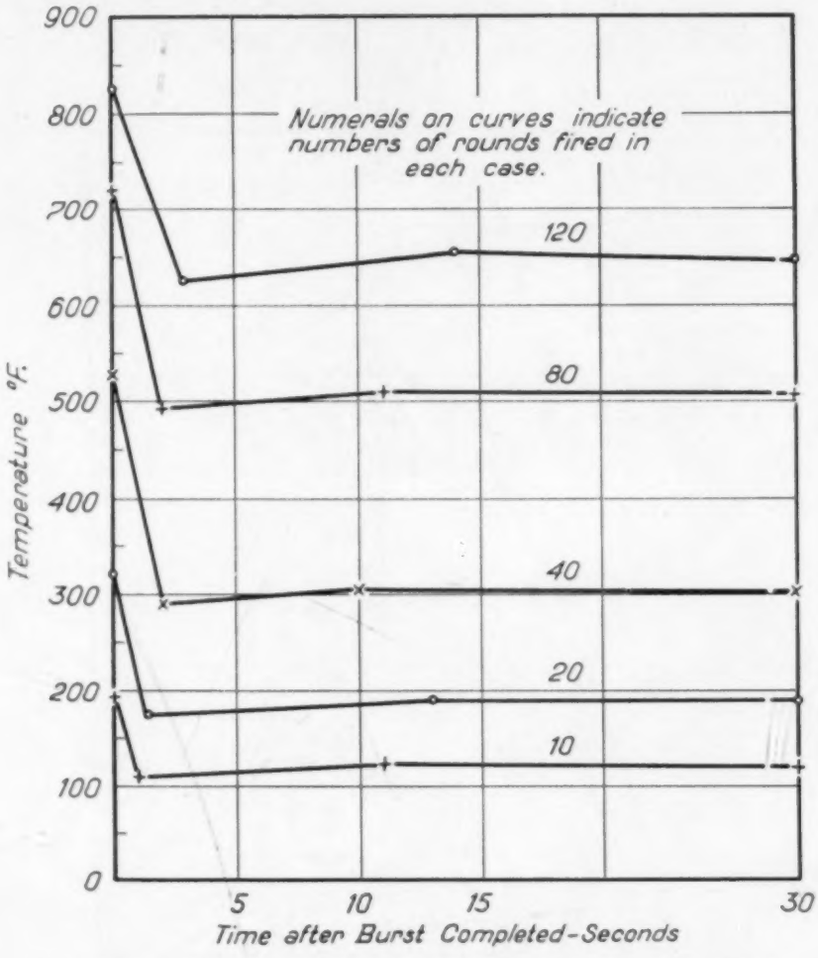


Fig. 6—Temperature Rise in Machine Gun Barrels. Showing Effect of Different Lengths of Bursts—After the Burst Was Completed.

ture for martensite. As a final check, Lester ran an X-ray diffraction spectra analysis of the layer and also on a nitrided alloy steel. The distortion of the lattices was the same in each case.

From this brief review of the literature, it is apparent that both the carburization and nitriding theories have had able support. They are entirely opposite in nature and much discussion has arisen as to which is the better explanation of the layer. The following data and discussion will help to clarify this situation and indicate the actual temperature conditions found in the barrel at the bore surface.

The Present Investigation

The work done during the present investigation consisted of two parts. The first part was a study to determine which of the two theories was correct. The second part was an investigation which had as its aim the reproduction of temperature conditions within the

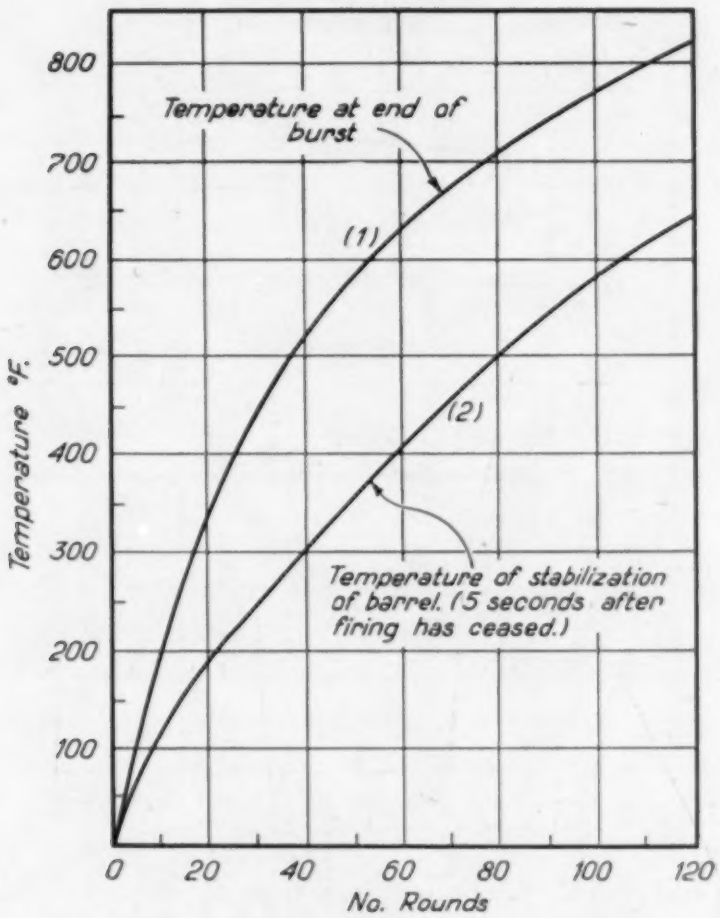


Fig. 7—Temperature Rise in Machine Gun Barrels. Showing Relationship Between Different Lengths of Bursts of Fire Measured in Rounds.

barrel. This was done in order that the temperature of reaction might be ascertained.

Checks upon the Theories—The process of checking the theories was essentially simple. A metallographic study was made of various specimens from machine gun barrels in an effort to determine the nature of the layer. The specimens were magnified as much as 2000 diameters for this study.

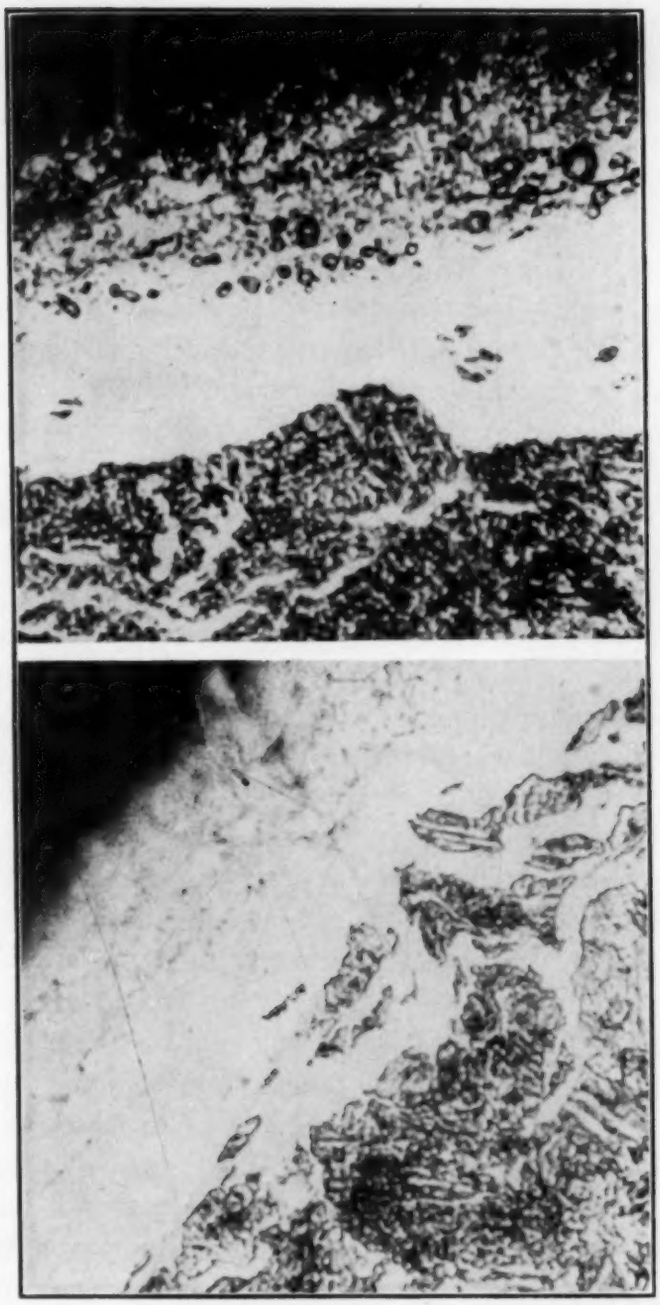


Fig. 8—(Upper) Case Nitrided at 1100 Degrees Fahr. (595 Degrees Cent.) for 12 Hours. × 1000.
Fig. 9—(Lower) Case Nitrided at 1000 Degrees Fahr. (540 Degrees Cent.) for 12 Hours. × 1000.

After the metallographic work on the used barrels was completed, some barrels were heat treated at 400 degrees Cent. (750 degrees Fahr.) for 1 hour and then slowly cooled. This was an attempt to determine whether the white layer did decompose at the higher temperatures.

A final check consisted of taking X-ray diffraction spectra of the gun barrel layer. These results were then checked against those obtained by Lester.

Determination of the Temperature of Formation—After the nature of the layer was discovered, it was thought advisable to conduct experiments for determining the temperature at which this layer was formed. This was done by nitriding samples of gun steel under various conditions. The temperatures used varied from 480 to 650 degrees Cent. (900 to 1200 degrees Fahr.). The specimens were cooled at various rates, in order to reproduce the cooling rates of the barrel. The photomicrographs from Figs. 8 to 11 show the various types of layers formed under these conditions.

Discussion of Results

All metallographic evidence obtained tends to support the nitriding theory as advanced by Lester. In Fig. 2 it will be seen that there is an indistinct suggestion of a needle structure, but nothing definite. Such a structure is a characteristic of both nitrided and martensitic areas. A martensite, however, would show a much more distinct needle pattern at the high magnification used. It will also be noticed that there is a very definite tendency for the layer to follow the surface into the cracks. This is a tendency in nitrided cases; and this tendency is clearly shown in Fig. 4 where the layer is well within the crack. It is entirely evident that the layer occurs within the cracks, but it is also known that this barrel was kept at a temperature of 400 degrees Cent. (750 degrees Fahr.) during its entire firing period. The presence of the white layer after such firing conditions points to one conclusion, that the white layer is a nitrided product. Martensite would never have remained or even formed at this temperature. A nitrided case, on the other hand, would not decompose at 450 degrees Cent. (840 degrees Fahr.). On the basis of metallographic evidence, then, it seems that the white layer is a nitride solid solution.

It would be incorrect, however, to accept or reject a theory on the basis of metallographic evidence alone. For this reason it was decided to check the metallographic results with evidence from heat treatments. Several sections of the gun barrels were heated in an electric furnace for one hour at 400 degrees Cent. (750 degrees Fahr.). They were furnace-cooled to eliminate any quenching action.

Such a treatment would completely break down any martensite formation and the layer, if it had been martensite, should be darkened. However, it was discovered that the layer was still white. Such a layer is shown in Fig. 5.

At this point it may be well to consider the possibility of a martensite formation by rapid cooling as proposed by De Sveshnikoff, since nitrides would not form if martensite were present. De Sveshnikoff argued that the large mass of metal surrounding the bore surface was sufficiently cool to allow for a rapid quenching effect on the bore surface. This fact, together with the definite increase in the carbon content, would cause the layer to be martensitic in nature. If the large mass were sufficiently cool De Sveshnikoff's theory might hold true, but data recently obtained from the Ordnance Department prove that the cooling process is a slow one. Figs. 6 and 7 are charts of these data. These charts show how barrels cool as regards temperature (Fig. 6), and also the temperature drop from the maximum to a stabilization point about 15 seconds after firing has ceased. It will be seen from Fig. 7 that the maximum temperature drop is only 175 degrees Fahr., and that the stabilization temperature is not low enough to allow any martensite to form.

A final check was made by the use of the X-ray. An X-ray diffraction pattern was obtained from the layer. The values of lattice distortion calculated from this pattern checked closely with those given by Lester. He obtained a lattice enlargement of the alpha iron of 0.5 per cent, while the results of this research gave a 0.49 per cent distortion. The enlargement of 0.50 per cent was exactly that obtained by Lester in a similar analysis of a nitrided layer on a chromium-aluminum steel. These results also indicate the layer in the gun barrel is a nitride.

It is believed, from the evidence presented, that the white layer is a solid solution of nitrides. The nitrogen is in solution in both the ferrite and austenite; this explains the glass hardness of the layer. This theory is in agreement with the one presented by Lester, and the results of the investigation check his.

After the nature of the layer was determined, it was decided that an attempt should be made to determine the temperature of nitriding in the barrel. This was accomplished by nitriding specimens of the original gun steel at various temperatures and varying the rate of cooling.

The cases formed at the different temperatures varied in nature,

but varying cooling rates showed little effect. It has been, therefore, decided to show only a representative photomicrograph of each

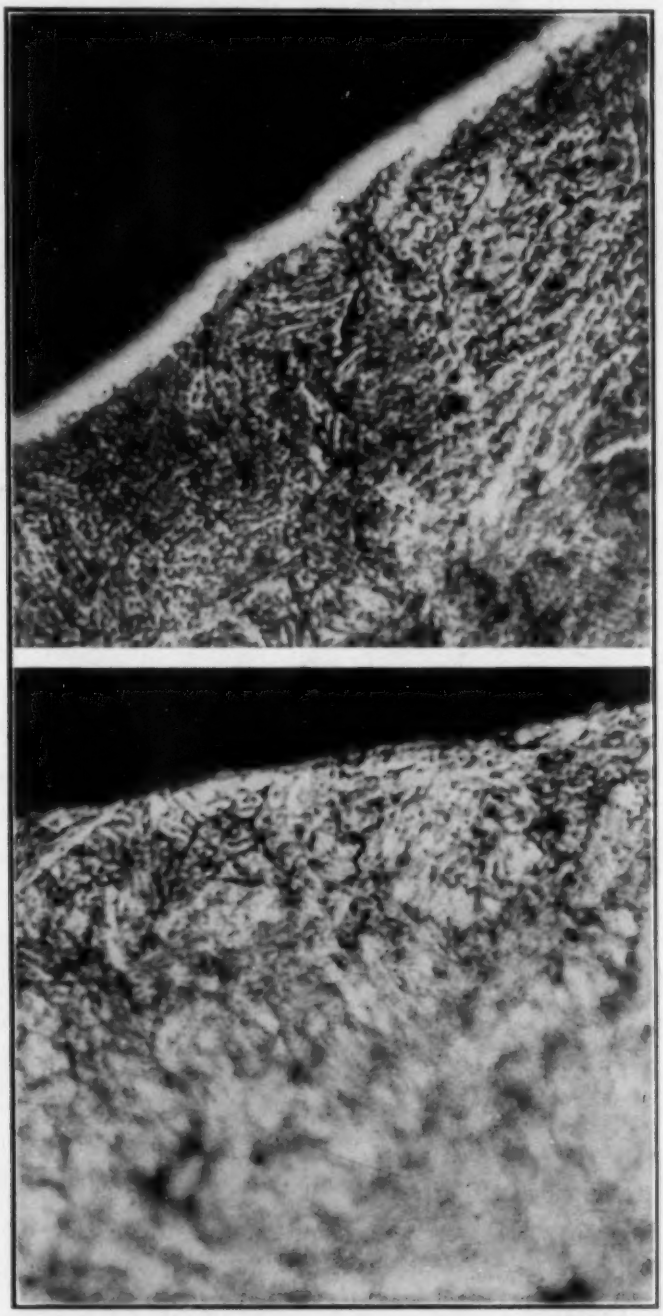


Fig. 10—(Upper) Case Nitrided at 900 Degrees Fahr. (480 Degrees Cent.) for 15 Hours. × 1000.
Fig. 11—(Lower) Specimen, Originally Martensitic, Nitrided at 900 Degrees Fahr. (480 Degrees Cent.) for 15 Hours. × 1000.

temperature. The proper procedure to test for layer duplication is to compare Figs. 8, 9, and 10 with Fig. 2. From a comparison of

these photomicrographs it is possible to determine the temperature of nitriding in the gun barrel.

Fig. 8 shows a case nitrided at 595 degrees Cent. (1100 degrees Fahr.). It can be seen that there is a definite decomposition of the case at this temperature. Since there is no such decomposition in the layer in Fig. 2, it can readily be seen that 595 degrees Cent. (1100 degrees Fahr.) is too high. An inspection of Fig. 9 shows that decomposition is still present. This fact precludes this temperature. When Fig. 10 is compared with Fig. 2 a striking resemblance is found. There is no decomposition at 480 degrees Cent. (900 degrees Fahr.). The layer is uniformly dense; it is also as white as the layer in the gun tube. A scratch hardness test showed they were equally hard. From a metallographic point of view, it seems that the layer may be duplicated in the laboratory at 480 degrees Cent.

While the temperature of formation seems low, in view of the theoretical flame temperature of 2800 degrees Cent. (5070 degrees Fahr.), there seems to be a satisfactory explanation for this. It must be remembered that the actual flame temperature is always considerably lower than the theoretical flame temperature. This would tend to lower the temperature of nitriding considerably.

Another factor which would lower the temperature of the bore surface is the poor heat transfer coefficient of a gas film. Such a film would undoubtedly form at the bore. This film would require a large temperature drop to allow heat to pass from the turbulent gases to the metal surface. This means that the temperature of the metal is much lower than the actual temperature of the gases.

It must also be remembered that there is quite a mass of metal surrounding the bore surface. This mass abstracts heat at a fairly rapid rate from the surface and tends to keep the surface metal cooler. It is true, however, that a rapid quench is not involved.

A final argument is provided by Fig. 12. This chart shows that, at a distance of 0.029 inch from the bore surface of a water-cooled gun, the temperature is approximately 430 degrees Cent. (810 degrees Fahr.). Allowing for a high temperature drop across the metal from the bore surface to the thermocouple, and also a lag in readings, it is entirely possible to have a nitriding temperature of 485 degrees Cent. (900 degrees Fahr.). Due to the high pressures it might conceivably be somewhat less, but it certainly is no greater than 485 degrees Cent. (900 degrees Fahr.).

On the basis of the literature and the results presented, it is

concluded that the white layer formed during the erosion of machine gun barrels is a solid solution of nitrogen and nitrides in austenite

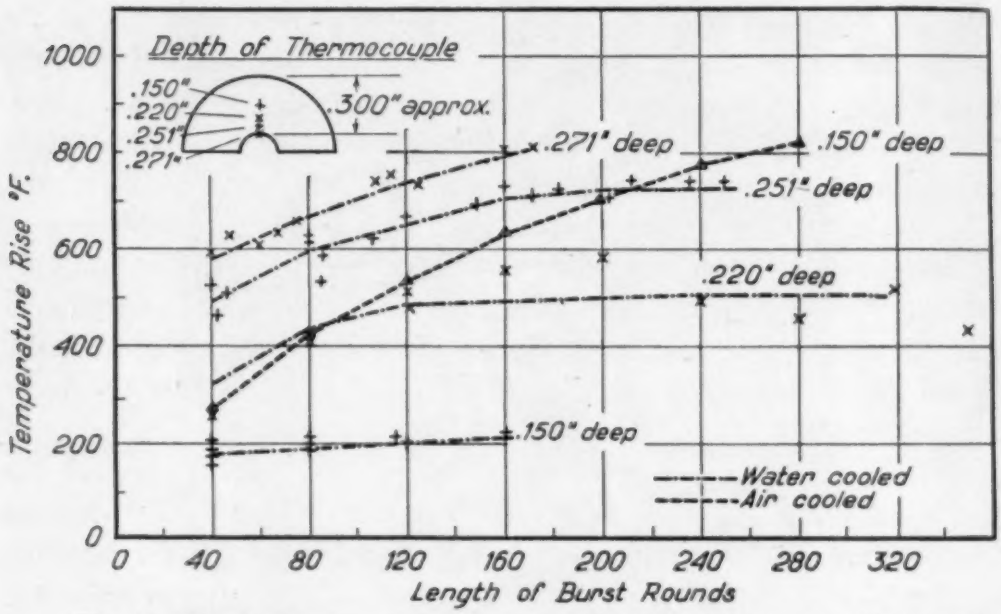


Fig. 12—Rise in Temperature at Various Points Across Section of Machine Gun Barrels, When Long Bursts are Fired.

and alpha iron. The nitriding seems to take place at a temperature of 485 degrees Cent. (900 degrees Fahr.).

Acknowledgments

The authors wish to express appreciation to the Ordnance Department of the Army, to Col. G. F. Jenks, Major R. E. Hardy, and Prof. Lars Thomassen for their suggestions and assistance.

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DISCUSSION

Written Discussion: By Peter R. Kosting, chemical engineer, War Department, Watertown Arsenal, Watertown, Mass.

The Ordnance Department appreciates, I am sure, the interest taken in studying some of its peculiar problems.

It must be emphasized that the white layer described in this paper came from one type of machine gun fired under special conditions, and that the graphs given in Figs. 1, 6, 7, and 12 refer to another type of machine gun fired under very different conditions. Care must be exercised in reading some of the graphs to distinguish what the abscissae represent—number of rounds or number of rounds per burst.

At the Watertown Arsenal, technique has been developed to bring out the structure of the white layer. Miss M. R. Norton, working on machine gun barrels, has obtained some excellent photomicrographs showing acicular structure and the presence of several layers. More recent work on cannon has shown the necessity for etching to reveal the complex structure, and it now appears that there are present in the portion considered as the white layer, up to three layers and four phases, one of which "tempers" when heated to 700 degrees Fahr. X-ray work to identify the compounds formed is in progress. There appears to be no reason to doubt that there are actual nitrides of iron present. It should be mentioned that De Sveshnikoff observed up to 100 per cent loss in nitrogen as well as an increase in nitrogen in other cases. The authors have shown that nitriding with ammonia at 900 degrees Fahr. produces a structureless layer the same as is observed in the gun barrel under the microscopic technique used. The ratio of H_2 to NH_3 at the nitriding surface and the temperature and pressure materially affects the results obtained. I cannot agree that the temperature of the bore surface of machine gun barrels must be limited to 900 degrees Fahr. to form nitrides similar to those formed in ammonia. Any theory of erosion will not be adequate unless it explains the mutual effects of CO, CO_2, CH_4, N_2, H_2, H_2O, temperature, pressure and time.

Written Discussion: By Victor Stefanides, metallurgist, Illinois Tool Works and Shakeproof Lock Washer Co., Chicago.

The writer should like to suggest that the authors give some consideration to the H_2 and the H_2O gases present in the products of combustion. These two gases may play a more important role than they are being given credit for. The austenite when formed in presence of H_2O which evidently breaks down, and the oxygen goes into solution with the carbides, forms a more stable austenite which is hard to break down, requiring higher temperatures than austenites without the oxygen in solution.

Methane is a very potent carburizer but of course at higher temperatures than those investigated by the authors.

Hydrogen may play an important part in cracking the layer. The writer has investigated some lock washers which were very brittle after electroplating. On investigation of this problem it was disclosed that when the washers received a thorough tempering so that the stresses were relieved, after electroplating such washers were found satisfactory. However, washers which did

not receive a thorough tempering and were in a stressed condition, on electroplating were very brittle even after the customary baking treatment. Therefore it was concluded that hydrogen embrittlement is detrimental only in cases when stresses exist. The hard layer in a gun barrel may be a fertile field for the H_2 to do damage in.

Hydrogen may play another important role in cracking the layer. When hydrogen diffuses into steel it will combine with carbon, especially when heat is available, to form methane. The volume of methane would be so tremendous that it actually would burst the layer open. The top layer of Fig. 8 suggests some gas being present.

The writer makes these suggestions as a possible field of further investigation, because the evidence in support of nitride formation is not convincing. The writer wishes to congratulate the authors on handling this problem so efficiently.

Written Discussion: By H. H. Lester, War Department, Watertown Arsenal, Watertown, Mass.

One is naturally pleased to have his experimental results verified. Mr. Snair and Professor Wood have contributed materially towards establishing the theory which states that the white layer is essentially a nitrided case. The probable influence of nitrogen in its formation was suggested first by A. O. Knight of Watertown Arsenal in 1917. However, the theory was really established by the elaborate research of H. E. Wheeler of the same laboratory and published in the A.I.M.E. *Transactions* of 1922. The writer, in 1929, published data showing the essential similarity between a commercial nitrided case and the white layer. These have been verified in the present paper.

The Wheeler theory seems to be fairly well established. However, it should be evident that the case at the bore of a gun tube is probably more complex than that produced in commercial nitriding operations. It has been pointed out by the authors that pressures and temperatures in the powder gases run very high. Also carbon, hydrogen, and oxygen are present as well as nitrogen. De Sveshnikoff has shown that there is a considerable carbon pickup and has explained the white layer on this basis. It is known that hydrogen diffuses through steel even more readily than carbon. It is not known what role, if any, is played by hydrogen in producing hardening. It is assumed to be an unimportant factor in the white layer as found because the structure seems to be unaffected by thermal treatments that would drive off hydrogen. However, the above is not a conclusive test. It may be in solution in the surface layers of the steel in actual service conditions. The possibility for this is the greater because, except for machine gun barrels where there is sustained fire, the temperature of the metal is quite low except for a layer at the inner surface only a few thousandths of an inch thick. The hydrogen diffuses much beyond this layer and, in the region where the temperature of the metal exceeds 300 degrees Cent. (570 degrees Fahr.), would certainly be in solution in the steel with consequent hardening.

The influence of oxygen has been dismissed as not important in the white layer structure because it has been supposed that oxygen is effective principally in forming oxides that are carried out with the powder gases. It would thus be a factor in rapid erosion of the powder chamber, but not an important

contributor to the layer structure. Possibly this picture is too simple. At least there is need for further study of the effect of oxygen based on definite experimental evidence.

There is the question of the effects of nitrogen. Its importance in the case structure is not doubted. But what compounds are formed and where are these located in the layer? To what extent are these or is nitrogen itself in solution in the iron crystals? How do these structural features affect the properties of the layer? These and other questions are pertinent ones that must be answered.

Finally, there is an intriguing question as to whether or not the hardened layer should shorten service life or should it lengthen it? It has been assumed that spalling of this layer is an important factor in erosion. However, spalling occurs in a late stage of the life of the gun. In the early stages at least the hardened layer which extends considerably beyond the thin skin that is raised to high temperatures should tend to prevent erosion in the portion of the tube beyond the powder chamber. In the powder chamber itself, where oxidation of the steel is probably an important factor in erosion, the effect of the nitriding should tend to prevent oxidation. Nitrided layers are known to be highly resistant to oxidation at low temperatures. The presence of the nitrogen at elevated temperatures should be expected at least to retard oxidation.

An extended study of the white layer is under way at Watertown under the direction of Dr. P. R. Kosting. It is hoped that new light will be thrown on some of the questions involved. Also, it is hoped that the authors will be encouraged to continue their researches in this interesting field.

Oral Discussion

O. E. HARDER:[1] We have had to do some work which seems to have some bearing on this particular problem. In the case of certain steels in the service for which they were used they were nitrided. The service involved rapid heating and then cooling, the heating being up to probably 1500 degrees Fahr. at the surface, and I venture to say that the surface of the barrel in the firing of these guns is probably considerably higher than the temperature noted by the thermocouples.

We found that with a given steel if the surface had been nitrided it was much more sensitive to heat checks than if that same steel had been heat treated to the same hardness and not nitrided. So our experience indicates that at least in some steels if there is a thin nitrided surface it is much more sensitive to heat checking by rapid heating and cooling than when that same steel is not nitrided. That seems to fit in with the picture which the authors of this paper presented.

L. S. BERGEN:[2] It is interesting to recall some German work which appeared two years ago on the wear of gears at atmospheric temperature and in which the investigators concluded that the wear in that case was also nitriding. Whether that has any correlation with Mr. Snair's work, I do not know, but

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[1]Assistant director, Battelle Memorial Institute, Columbus, Ohio.

[2]Metallurgist, Crucible Steel Company of America, New York.

it at least indicates that nitriding is becoming more important in any consideration of wear we might have, even at room temperatures.

Authors' Reply

The authors are appreciative of the discussion which has been submitted in connection with this paper. It is quite evident that the problem has more ramifications than appeared to be the case in the beginning and also that other observed surface effects may have characteristics in common with those noted in the case of eroded machine gun barrels.

Both Dr. Lester and Mr. Stefanides dwell at some length upon the possible effects of hydrogen. This is an aspect of the problem which was not studied by the authors. It is easy to believe that hydrogen may have quite definite effects upon the mechanical properties of the metal but it would seem that any effects upon the microstructure would be, at least, indirect. It is the feeling of the authors, that, while Dr. Harder did not state under what conditions the steels to which he referred were heated and cooled, it is this factor which is of most importance in causing the surface cracks and in some cases the complete destruction of the rifling.

The results of the work being done at Watertown Arsenal as outlined by Dr. Kosting are most interesting and give promise of ultimately leading to a solution of the problem. The inability of previous workers to resolve the structure of the white layer has been the principal stumbling block. The existence of layers within the white layer suggests the structure which is observed in ordinary nitrided surfaces. It was not the purpose of the authors to suggest maximum or minimum temperatures which exist during firing cycles, but merely to ascertain whether or not a white layer could be produced under conditions of temperature which might reasonably exist during the firing of the gun.

In connection with the statement of Mr. Bergen it is interesting to note that one of the authors has been advised, since the presentation of the paper, that a somewhat similar case of surface effect has been observed on steel cable which has been subjected to wear.

THE INFLUENCE OF MICROSTRUCTURE UPON THE PROCESS OF DIFFUSION IN SOLID METALS

By Frederick N. Rhines and Cyril Wells

Abstract

Studies of structural changes accompanying diffusion, anisotropy of diffusion, and intergranular diffusion have been made using previously published and new data. The methods used in obtaining these data have also been discussed.

Columnar grains form in systems involving a phase change. Recrystallization, grain growth, and twinning may be induced in a single phase by diffusion if the specific volume changes caused by a movement of solute are sufficiently large.

Previous investigators have presented considerably more evidence of an anisotropy in non-cubic than in cubic metals. New evidence of an anisotropy of diffusion in cubic metals (copper-zinc system) is given, and it is shown that anisotropy may depend on the concentration of solute.

Intergranular diffusion in metal systems seems to be faster than intragranular diffusion. Contrary to the belief of many, it has been shown that carbon does not diffuse faster through γ iron grains than along grain boundaries.

IT has been recognized for some time that the rate of diffusion in solid metals may vary with the amount and kind of impurities, with the grain size, with different relative orientations of the solvent crystals, and with such structural changes as phase transformations, grain growth, recrystallization, and twinning. Nevertheless, diffusion coefficients for metal systems have commonly been measured without regard for the possible influence of structural characteristics, chiefly because of a lack of adequate theory concerning the nature of structural effects and of experimental methods. As a result, the values

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obtained have often been averages of the diffusivity constants for undefined sets of heterogeneous conditions.

In 1936 the literature on diffusion was reviewed and appraised by R. F. Mehl (1)[1], who pointed out the unsatisfactory state of this particular branch of the subject and the need for further investigation. Several valuable contributions have appeared in the meantime.

It is the purpose of the present paper to present a group of new observations and to re-examine some of the published data with particular regard to the experimental methods that have been employed. The subject matter will be grouped under three headings, namely, structural changes accompanying diffusion, the anisotropy of diffusion, and intergranular diffusion.

Structural Changes Accompanying Diffusion

The structural changes that occur in a binary alloy system during diffusion in the solid state may be divided into two classes: first, the columnar grain formation usually associated with the appearance of a new phase; and second, recrystallization, grain growth, and twinning, occurring during diffusion in the absence of any phase transformation. It is important that the alterations of the microstructure that appear during the period of heating or cooling between the temperature of diffusion and room temperature be distinguished from those induced at the diffusion temperature, because the former are associated mainly with temperature changes, while the latter are associated with concentration changes alone.

Because the structural alterations accompanying diffusion occur under conditions that make their continuous experimental observation difficult or impossible, it is impractical at the present time to evaluate their quantitative influence upon the rate of diffusion. It is possible, however, to observe by microscopic means the kinds of changes that take place.

When the constitution of a binary diffusion system is such that the penetration of the solute material must be accompanied by the formation of a new phase, it is commonly observed that the crystals of the new phase grow continuously from their sites of origin in the general direction of the penetration thus forming columnar grains (Fig. 1). Ordinarily the individual crystals extend across the entire zone of the new phase, but under certain circumstances, presumably

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

when the rate of formation of the new phase is greater than that of the growth of the crystals, a more or less equiaxed grain structure is produced. Since the subject of columnar grain growth has been critically reviewed in a recent paper by D. H. Rowland and C. Upthegrove (2), it will be given no further consideration here.

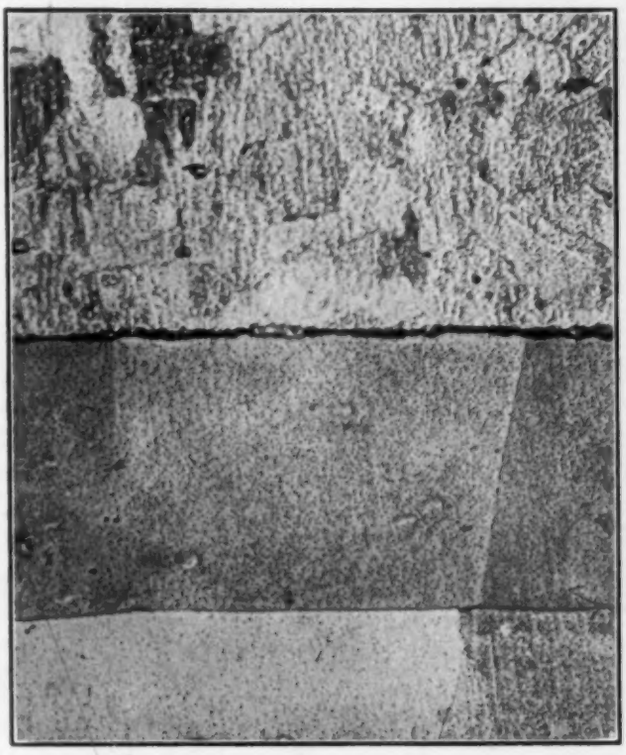


Fig. 1—Columnar Grains of γ and of β Brass Formed by the Diffusion of Zinc into Copper. The Polycrystalline Copper was Heated for 150 Hours at 400 Degrees Cent. with Chips of a 65-Per Cent Zinc, 35-Per Cent Copper Alloy. Top Band, Copper and α Brass, Center Band β Brass, Bottom γ Brass. Etched with CrO_3 in HNO_3. × 250.

The occurrence of grain growth, recrystallization, and twinning in single phase diffusion systems has received less attention, but there are enough definite examples (17) to establish the existence of the effects. The present authors have found definite evidence of all three of these types of changes taking place during the diffusion of zinc in α-brass. Parallelopiped-shaped samples were cut from very coarse-grained copper in such a manner that each sample was composed of two copper crystals with the mutual boundary lying nearly perpendicular to four of the outside surfaces. These were fully annealed and etched to insure the absence of recrystallization or residual stresses and were then packed in 70-30 brass chips in a sealed con-

tainer and annealed for one week at 775 degrees Cent. (1425 degrees Fahr.).

Upon examination, the cross sections of several of the samples exhibited a remarkable type of displacement of the grain boundary (Figs. 2a and 2b). The two grains seemed to have grown into each

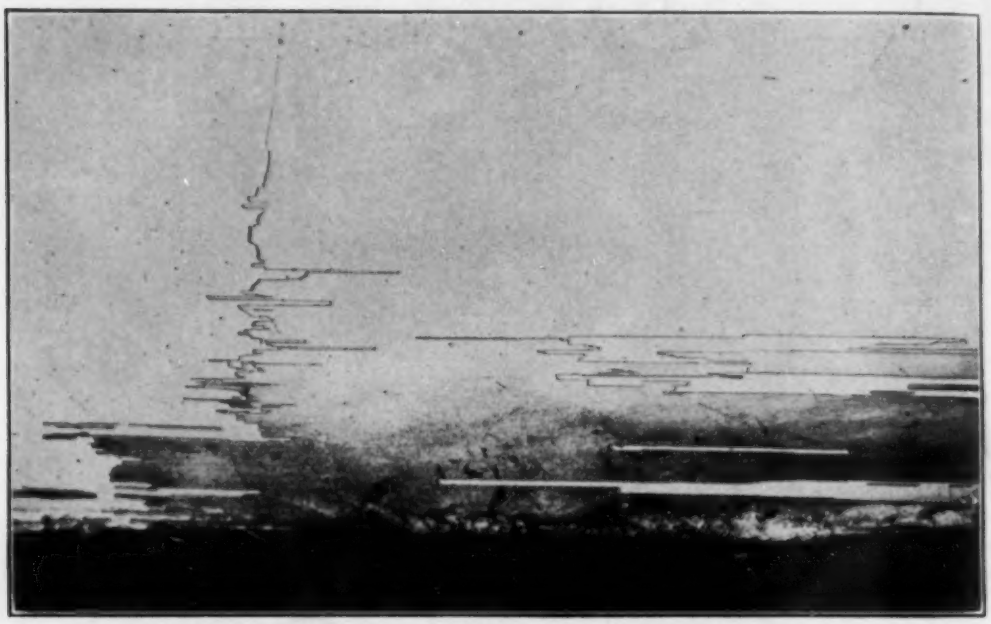


Fig. 2a—Shows Movement of Grain Boundary (Originally Almost Straight) Between Two Copper Crystals Upon the Penetration of Zinc in a Direction Parallel to Boundary. The Copper Bicrystal was Heated with 70-30 Brass Chips for One Week at 775 Degrees Cent. Ammonia and Hydrogen Peroxide Etch. × 100.

other alternately in long narrow bands. It was established by X-ray determinations of orientation that the two copper crystals did not lie in a twinned relationship. Evidently the distortion of the copper lattice by the penetration of zinc had been sufficient to induce grain growth that proceeded in steps as the zinc progressed in from the surface. It may be significant that this behavior has been observed by the authors in only these samples presenting a single grain boundary nearly parallel to the direction of the zinc penetration; yet there can be little doubt that this is a real case of grain boundary migration (grain growth) induced by diffusion.

At the corners of several of the samples, and in some samples at the original grain boundary, new crystals appeared (Figs. 3a and 3b). These small crystals were absent in the fully annealed copper samples prior to diffusion and may, therefore, be taken as evidence of recrystallization induced by diffusion.

The same photomicrographs (Figs. 3a and 3b) show the pres-

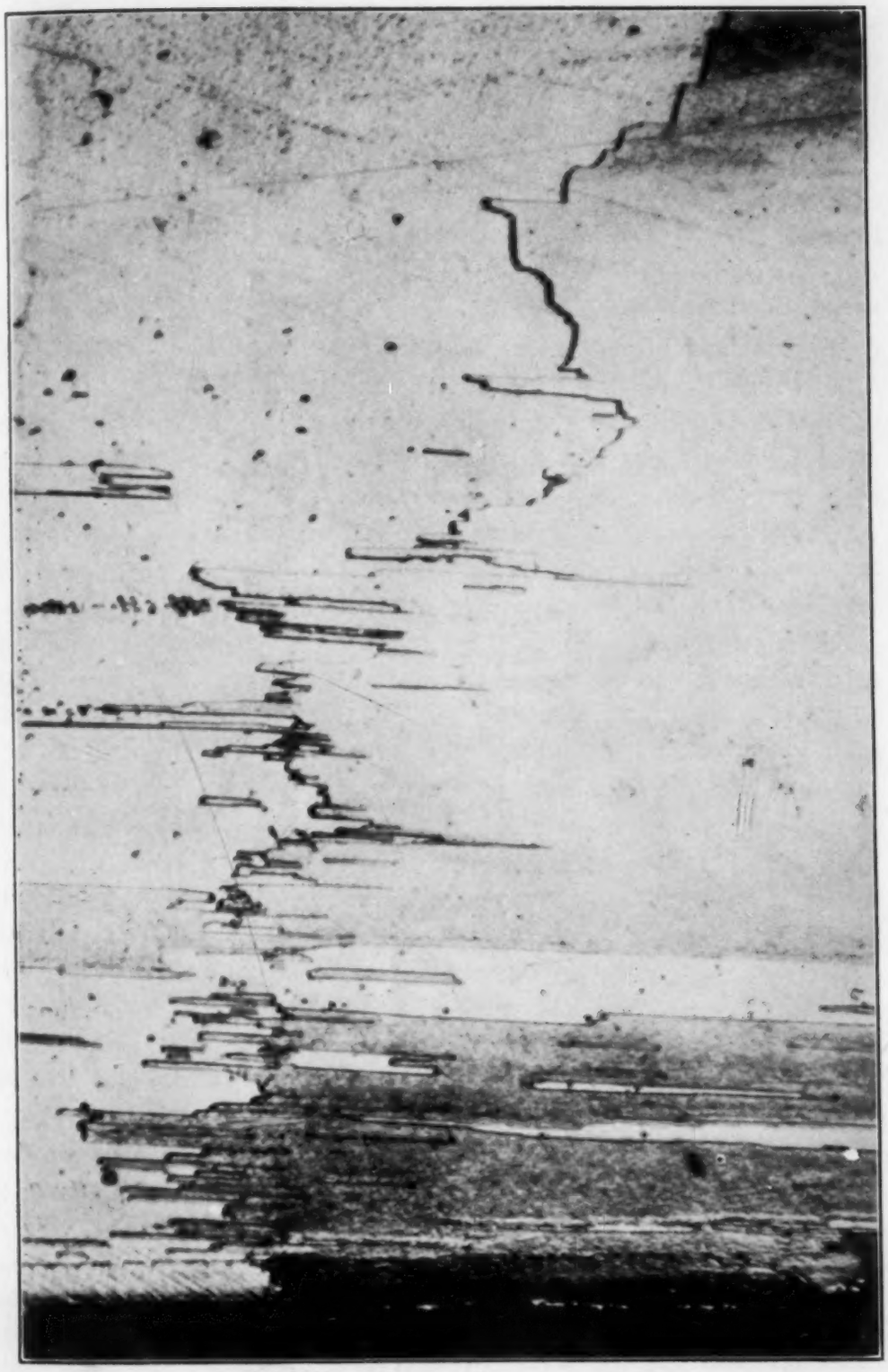


Fig. 2b—A similarly Treated Sample as Fig. 2a at × 250. Shows More Clearly the Longer Narrow Bands Near the Surface and the Shorter Wide Bands Toward the Interior.

ence of several annealing twins, which, because they are terminated by the recrystallized grain boundary, must have formed late in the diffusion treatment. It is possible, of course, that they were formed during the relatively slow cooling from the diffusion temperature. Another example of twin formation was found in single crystals of zinc into which copper had been diffused at 300 degrees Cent. (570 degrees Fahr.) from an electroplate (Fig. 6b). The micro-section shown was prepared by cleaving the sample at the temperature of liquid air. This operation might well have caused the formation of twins, but since no twins were formed when undiffused pieces of the same copper-plated zinc crystal were cleaved by exactly the same method, it is at least possible that those shown were formed during the diffusion treatment. It is noteworthy that they extend far beyond the zone of the visible copper penetration.

When a solute, capable of materially expanding or contracting the crystal lattice of its solvent, enters by diffusion, a state of stress may be established between the zone of solute penetration and the undisturbed solvent. Since the temperatures employed in diffusion experiments are well above the recrystallization temperatures of metals, the conditions of stress and high temperature necessary for grain growth and recrystallization are met.

It is reasonable to suppose that the tendency of a given mass of metal to recrystallize or undergo grain growth or twin formation, when stresses have been generated by diffusion in this way, will depend chiefly upon the geometry and intensity of the stress, the temperature, and the physical nature of the alloy within the concentration range concerned. The type of stress distribution may be expected to depend upon the shape of the diffusion interface, whether curved or flat, and thus in some cases upon the shape of the specimen, as well as upon the nature of the grain structure of the metal, that is, the relative orientations of adjacent crystals and the size of the grains. While the intensity of the stress may be related to its distribution, it should depend in the main upon the specific volume gradient which is derived from the concentration gradient of the solute and the magnitude of the effect of the solute upon the lattice parameter of the solvent. Thus a steep concentration gradient might represent a small specific volume gradient in the event that the solute does not greatly affect the lattice parameter of the solvent, or conversely a small concentration gradient might represent a large volume gradient.

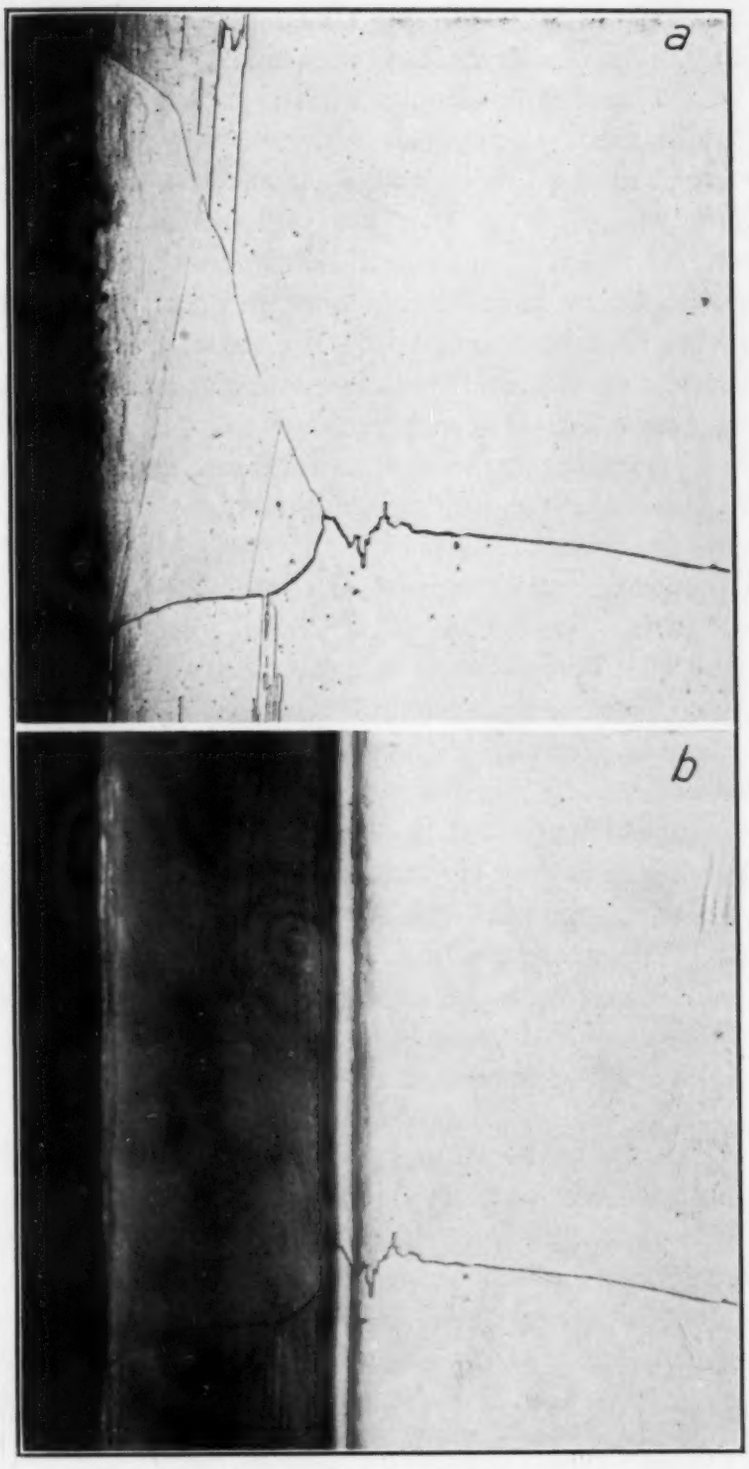


Fig. 3a—Similar to Fig. 2a Except that New Crystal Has Formed at Point Where Original Grain Boundary Met Surface. Some Grain Boundary Migration Just Above the New Crystal, and Two Twin Bands Across the New Crystal. Ammonia and Hydrogen Peroxide Etch. × 100.

Fig. 3b—Same as Fig. 3a Except that the Etch Has Been Permitted to Stain the Zone of High Zinc Concentration. The Limit of the Dark Band Lies at a Zinc Concentration of Approximately 20 Per Cent.

That relatively large volume changes favor the appearance of recrystallization is illustrated by the fact that no microstructural changes were observed in samples of iron into which chromium was diffused below the A_3 temperature, where only the α phase forms (Fig. 8), or in samples of iron into which nickel was diffused above the A_3 temperature, where only the γ phase is formed (18). An addition of 68 atomic per cent of chromium increases the lattice parameter of iron by only 0.011 Ångström units, and 39 atomic per cent of nickel expands it but 0.025 Ångström units, while only 24 atomic per cent of zinc increases the lattice parameter of copper by 0.061 Ångström units. Thus, the volume changes encountered in the copper-zinc system, where recrystallization was found, were much larger than in either the iron-chromium or the iron-nickel systems, where it was not found.

For any given temperature and composition of alloy, there is probably a limit of stress below which no microstructural changes will be induced. Thus it is to be anticipated that such changes are most likely to occur at an early stage in the diffusion process when the concentration gradient is steep and to cease as the gradient becomes flat. This view is supported by the structure shown in Figs. 2a and 2b, in which the bands of grain growth are generally narrower and longer near the surface of the sample, where the gradient was steep at first, and in which the grain growth seems to have stopped altogether at a point that may be identified with a zinc content of about 15 per cent, where the gradient has become less steep.

Anisotropy of Diffusion

An anisotropy in the rate of diffusion of a solute through a crystalline solvent will be most evident if the penetration is confined to a single solvent crystal, a single layer of crystals, or to a polycrystalline aggregate having a preferred orientation of its crystals. The effects of anisotropy will be nullified by the passage of the solute through a series of randomly oriented crystals. Of the methods that have been used for detecting the anisotropy of diffusion, most have involved the use of single crystals or single layers of crystals, and the advance of the solute has been observed by a wide variety of means, among which microscopic observation and chemical analysis have been common.

Unfortunately, the observation of anisotropy is complicated by

the possible appearance of a number of concurrently operating phenomena, some of which are likely to give a false impression of the existence of anisotropy, and others may conceal a real effect. Among the factors likely to cause an exaggeration or simulation of anisotropy are the crystallographic effects upon the rate of condensation and absorption of the solute at the entrance surface of the solvent, the influence of the relative orientations existing between the crystals of a newly formed phase and those of the initial solvent upon the rate of growth of the new crystals and upon the rate of discharge of the solute into the undersaturated solvent, and the influence of the crystal orientation upon the behavior of such penetration-depth indicators as microscopic etching effects, the appearance of Widmanstätten patterns, and the capacity to emit electrons. A real anisotropy may be nullified or partially concealed under certain experimental conditions by the existence of a large difference between the rate of diffusion along grain boundaries and within the crystals, by the lateral diffusion of the solute into adjacent crystals, by recrystallization and grain growth in a single-phase system, by certain types of preferred orientations, and by insensitive penetration-depth indicators.

Because of these factors, it is advisable to exercise caution in accepting as evidence of anisotropy such observations as the more rapid advance of a solute through certain crystals of a monocrystalline layer or the more rapid growth of certain columnar crystals in a polyphase system. Conversely, the absence of such effects should not be taken as proof of the absence of anisotropy; however, the writers choose to believe that large effects of the types mentioned are more likely to be the result of a true anisotropy than of any one of the other factors that have been listed above.

There are a number of instances of convincing evidence of an anisotropy of diffusion occurring among the non-cubic metals. W. Seith (3), by observing the rate of disappearance of a radioactive isotope of bismuth into stable bismuth demonstrated that at 269 degrees Cent. (515 degrees Fahr.) the rate of self diffusion of bismuth is approximately one million times greater perpendicular to the rhombohedral axis than parallel to it. At 200 degrees Cent. (390 degrees Fahr.) the rates in the two directions are about the same.

The rates of the diffusion of mercury into the hexagonal metals cadmium and zinc and of copper into zinc at 50 and 200 degrees Cent. (390 degrees Fahr.) were investigated by V. Bugakov and N. Brezhueva (4), who found the velocity to be greatest in the directions

lying in the basal plane and least in the direction perpendicular to the basal plane. At 50 degrees Cent. the effect was more pronounced than at 200 degrees Cent. (390 degrees Fahr.). This temperature dependence appears to be opposite in direction to that reported by W. Seith, but seems reasonable in view of the X-ray evidence of a decrease in crystal perfection at temperatures approaching the melting point. The experimental method consisted in observing the shape of the penetration zone emanating into a single crystal from a small point of the solute. Although there may be some reason for questioning the conclusions drawn from the experiments in which mercury was used, because of the introduction of a liquid phase, the observations upon the diffusion of copper into zinc appear to be fully acceptable.

Until recently instances of an anisotropy of diffusion in cubic metals have been lacking. R. M. Brick and A. Phillips (5) have now observed an apparent difference in the rate of penetration of copper into adjacent randomly oriented grains of aluminum and around the periphery of a single crystal of aluminum. The diffusion treatments were conducted at temperatures between 440 and 540 degrees Cent. (825 and 1005 degrees Fahr.), and the samples were quenched at the conclusion of the heating period. In order to indicate the depth of penetration of the copper the specimens were allowed to over-age at elevated temperatures below the diffusion temperatures, whereby a copper-aluminum compound was precipitated within the zone of copper saturation. By selecting various aging temperatures, the limit of precipitation was used to indicate the depth of penetration at a series of copper concentrations. The indications of anisotropy were found to be more pronounced at high than at low copper concentrations. These experiments may be subject to the objection that the indicator-precipitate forms a Widmanstätten pattern, the appearance of which can change with the crystallographic orientation of the surface of observation, but the differences in the depths of penetration were so large that it is difficult to account for them in any way except by the action of anisotropy.

A study of the anisotropy of the diffusion of zinc in α-brass has been made by the present authors. Three cylindrical samples were carefully machined from a cast single crystal of pure copper. The end faces of one sample lay nearly in the cube plane (100) of the copper crystal, those of the second in the octahedral (111) plane, and those of the third in the dodecahedral (110) plane. After an-

nealing to insure the absence of stresses which might lead to recrystallization the samples were placed with 70-30 brass chips in an evacuated and sealed silica tube and held at a temperature of 775 degrees Cent. (1425 degrees Fahr.) for one week. After cooling, each sample was mounted in a lathe and the end face turned off in layers suitable

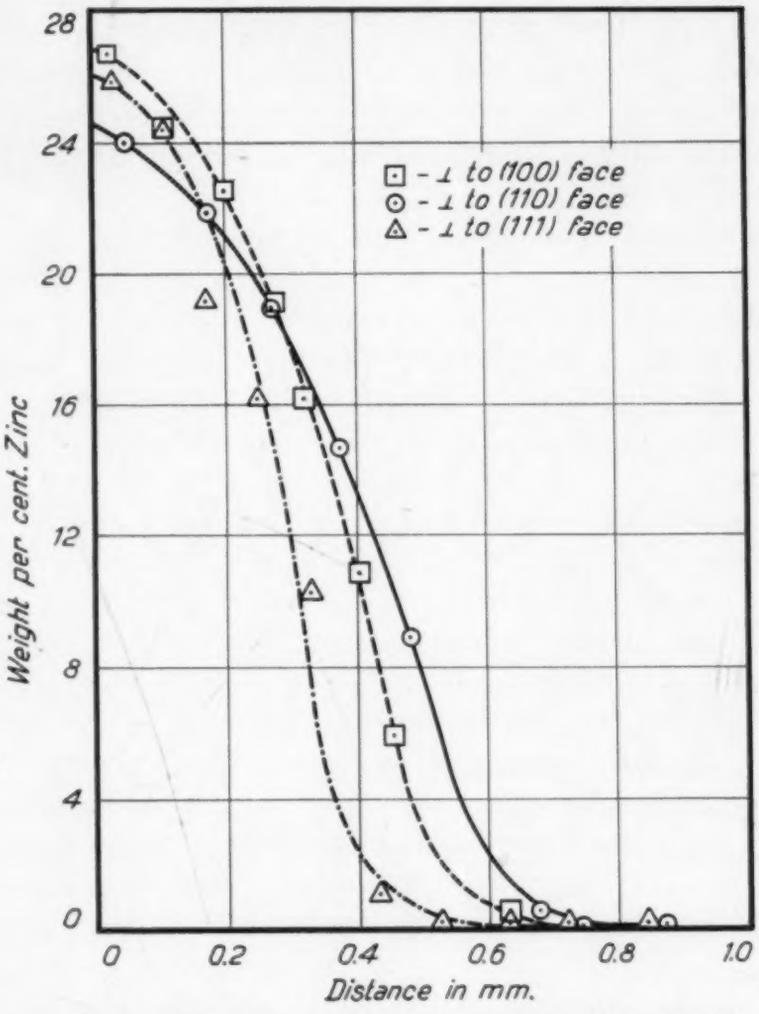


Fig. 4—Curves of the Penetration of Zinc into Single Crystals of Copper Perpendicular to a Cube (100) Face, a Dodecahedral Face (110), and an Octahedral Face (111). The Samples Were Heated with 70-30 Brass Chips for One Week at 775 Degrees Cent.

for chemical analysis. The depth of each cut below the original outside surface was measured with a surface micrometer, using as a reference the outside rim of the end surface that was not cut away. Concentration-penetration plots for the three samples are reproduced in Fig. 4. It is evident that at low zinc concentrations the diffusion has proceeded most rapidly in a direction perpendicular to the

dodecahedral face of the copper and least rapidly perpendicular to the octahedral face. At high zinc concentrations the curves are difficult to interpret and seem to show little difference in the rates of penetration.

It is noteworthy that R. M. Brick and A. Phillips found the directional effects to be most pronounced at high copper concentrations in the copper-aluminum system. This seems also to be true in the copper-zinc system. Since in both systems the diffusion coefficient decreases as the copper concentration rises, the maximum directional effects have occurred in both at the concentrations corresponding to the smallest values of the diffusion coefficient.

The methods available at present for computing the diffusion coefficient are unfortunately not applicable to the conditions of this experiment, because the zinc concentration at the surface of the specimen seems to have varied with the time in an indeterminate manner. The qualitative observation of the differences in the rates of diffusion in the three directions are dependable, however, for the maximum error in the measurements cannot have exceeded $\pm$ 0.025 mm. of distance and $\pm$ 0.25 per cent of zinc. The maximum possible error is thus only one-fifth as large as the differences shown at a zinc concentration of 5 per cent, thereby leaving little doubt that there is a real anisotropy of diffusion operating in this case.

The same samples were next sectioned perpendicular to their cylindrical axes and were polished and etched to reveal the depth of the zinc penetration around the cylindrical surfaces (Fig. 5). Surprisingly enough systematic variations in the widths of the bands were not detected even by the use of a microscope and high precision microcomparator. Probably the explanation lies in the fact that the inner limit of the zinc penetration marked by the etch lies at a depth of approximately 0.2 mm., at which point the penetration-depth curves of Fig. 4 are very close together. In any event, this observation illustrates the uncertainty of the micrographic method for the detection of anisotropic effects.

The single-phase bicrystal of Fig. 3b, which was treated by a similar procedure, shows no marked difference in the depth of penetration of zinc in the two crystals, but a very slight discontinuity in the etching limit can be detected.

Micrographic evidence of a difference in the rate of growth of the columnar crystals of β and γ brass upon a polycrystalline copper base has been sought in samples that were heated in the presence of

chips of a 65-per cent zinc, 35-per cent copper alloy (Fig. 1). Despite the fact that the β and γ crystals were growing throughout the diffusion period, it is conceivable that they might have exhibited anisotropy. There are, in fact, some systematic deviations in the

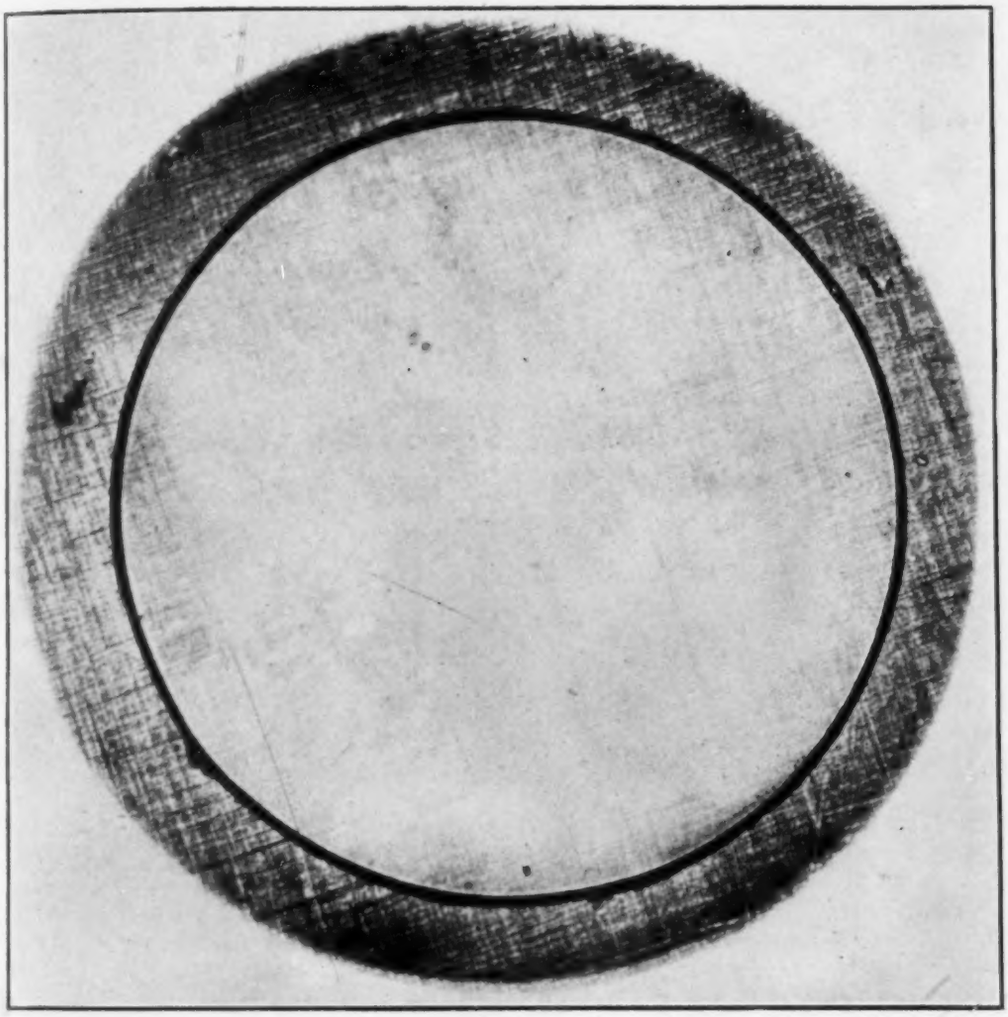


Fig. 5—Shows a Dark Band of α Brass Around the Cylindrical Surface of a Single Crystal of Copper into Which Zinc Has Been Diffused. The Sample is One of the Three Used in Deriving the Curves of Fig. 4. The Dodecahedral Face of the Crystal Lies in the Surface of Polish. Ammonia and Hydrogen Peroxide Etch. × 5.

location of both the γ-β and the β-α interfaces, but these are hardly of sufficient magnitude to justify any conclusions. Similar experiments have been conducted by L. Guillet and V. Bernard (6), C. F. Hudson (7), H. Weiss (8), and C. F. Elam (9) with the same results.

A peculiar type of irregular interface has been found between the η and ε phases of zinc single crystals into which copper had been

diffused from an electroplate (Figs. 6a and 6b). In places the interface appears to be made up of a series of more or less regularly oriented crystal facets. This structure suggests the operation of

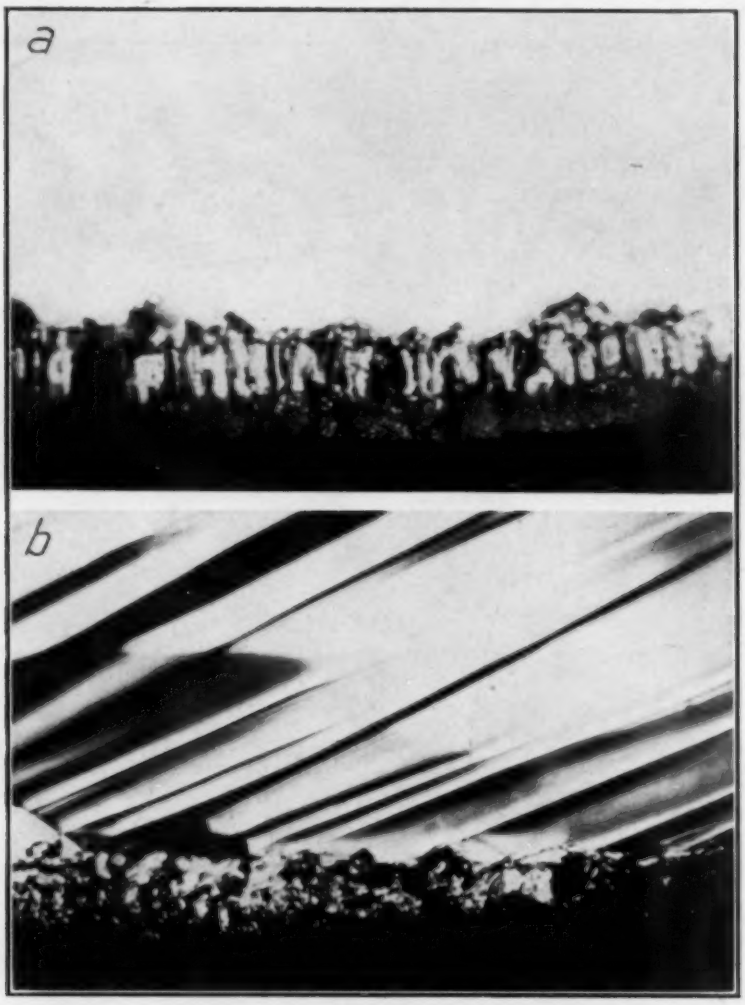


Fig. 6a—A Single Crystal of Zinc into Which Copper Has Been Diffused from an Electroplate. Sample Heated for 96 Hours at 300 Degrees Cent. Then Cooled to the Temperature of Liquid Air and Fractured Upon the Basal Plane. The Fractured Surface Unetched is Shown. × 325.

Fig. 6b—Same as Fig. 6a but Showing Twin Bands Extending into the Zinc Single Crystal.

some sort of anisotropy of growth of the ε phase, but this can be offered as evidence of an anisotropy of diffusion only with hesitation.

Samples of high purity iron into which chromium, nickel, nitrogen, and carbon respectively had been diffused were also examined for the presence of microscopic evidences of an anisotropy of diffusion. The phase transformations and volume changes that take place upon the cooling of these alloys make it difficult to ascertain the nature of

the structures existing at the diffusion temperature. Only in the case of the iron-chromium and iron-nitrogen specimens were suitable structures obtained (Figs. 7, 8 and 9), and these exhibited no marked evidence of any influence of crystal orientation upon the rate of diffusion. In Fig. 7, which shows the structure of an iron sample

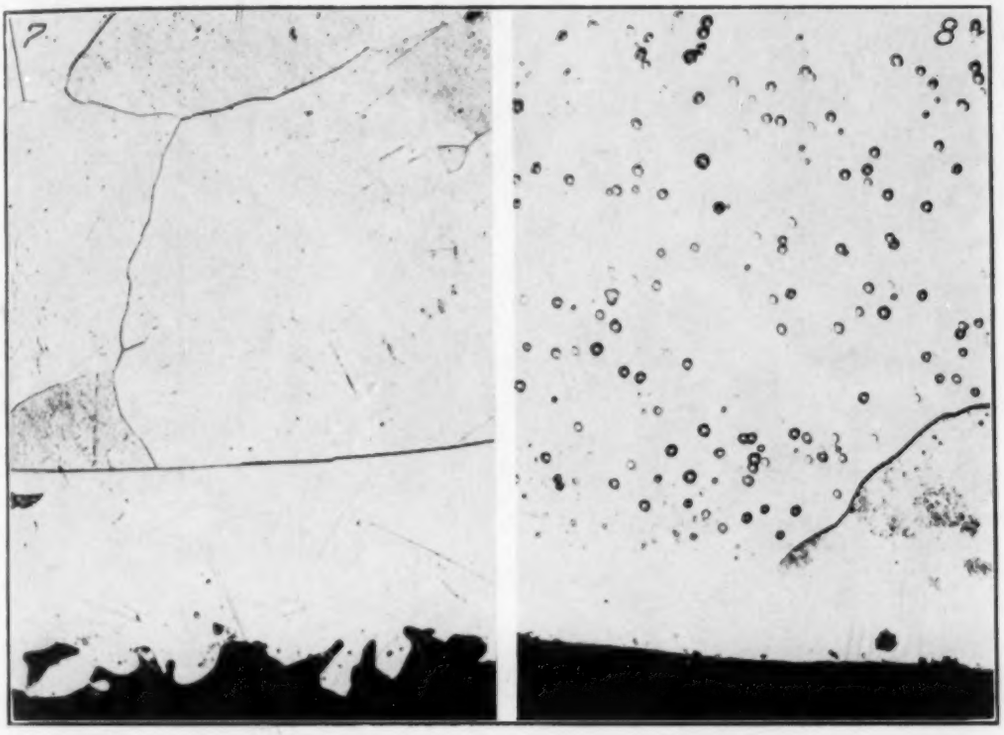


Fig. 7—High Purity Iron Which was Heated in Chromium Powder in Vacuum for 70 Hours at 1000 Degrees Cent. (Above the A_3 and Below the A_4 Temperature) and Quenched. The Bottom Band was the α Phase at the Diffusion Temperature, While the Upper Portion was the γ Phase Now Transformed to α. Nital Etch. × 100.

Fig. 8—Same Material as that Shown in Fig. 7 but Heated with Chromium Powder 200 Hours at 850 Degrees Cent. (Below the A_3 Temperature) and Quenched. The Entire Sample Remained α Phase Throughout the Treatment. Etched with 4 Per Cent Nital. × 100.

into which chromium was diffused above the A_3 temperature, the limit of the α-phase zone that existed at the diffusion temperature is clearly delineated by the etch. There are a few irregularities in this boundary corresponding to the location of the columnar α-phase crystals, but their magnitudes are very small indeed. The limit of the chromium penetration in the iron sample diffused below the A_3 temperature (Fig. 8) is not clearly shown by the etch and permits no conclusions whatever. An indication of the depth of penetration of nitrogen into two adjacent iron crystals is given by the location of a precipitate of iron nitride (Fig. 9), but the limit indicated in this way is again too uncertain for the detection of small differences.

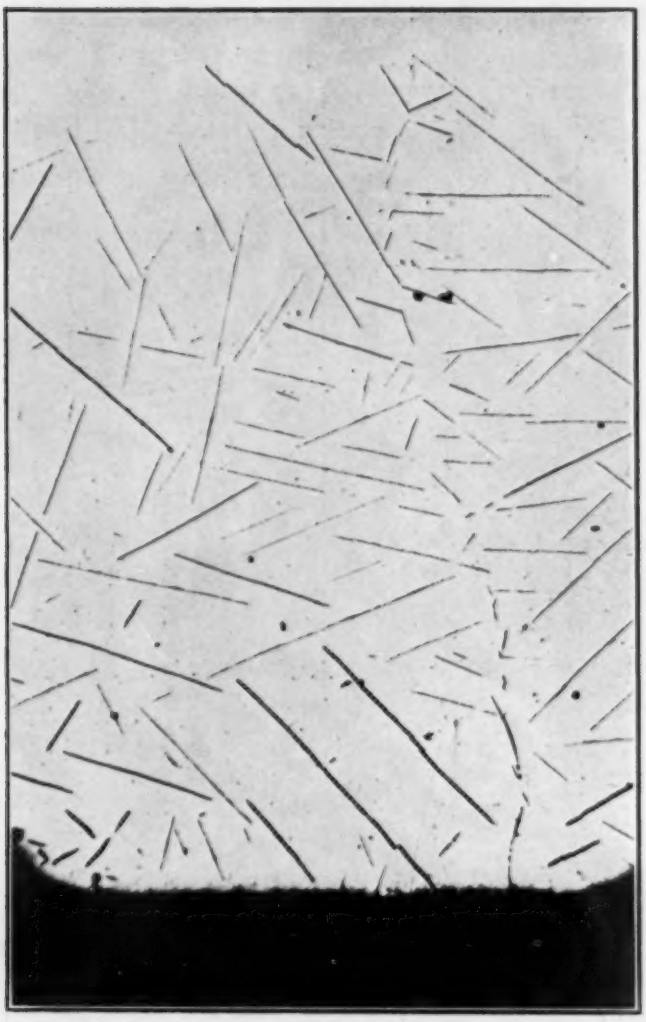


Fig. 9—Sample of High Purity Iron into Which Nitrogen Has Been Diffused By Heating in Ammonia Atmosphere for 30 Hours at 525 Degrees Cent.; Cooled at a Rate of 10 Degrees Cent. Per Minute. Depth of the Nitrogen Penetration Shown By Limit of Precipitation of the Iron Nitride. There Are Two Iron Crystals Separated By a Boundary on the Right-hand Side of the Photograph. Picric Acid Etch. × 100.

Intergranular Diffusion

It seems reasonable to suppose that there should be a difference in the rate of diffusion along grain boundaries and through the crystals of a polycrystalline metal, for the atomic arrangement at the grain boundaries must be quite different from that obtaining within the crystals and there is ample evidence of the dependence of the diffusion process upon atomic arrangement. If it be accepted that the grain boundaries are sites of lattice distortion comparable to those produced within crystals by cold deformation, it may further-

more be predicted that the diffusion is greater along the boundaries than within the grains, for it has been shown to be faster in deformed metals. The majority of the investigations (1) have led to the conclusion that the rate of intergranular diffusion is either greater or about the same as that of intragranular diffusion, but a few cases of the opposite effect have been reported.

For the study of intergranular diffusion there are two courses of experimental procedure available; first, the relative rates of advance of a solute along a grain boundary and within the adjacent crystals may be compared, or second, the difference in the rates of penetration of a solute through materials of various grain sizes but similar in all other respects may be observed.

There are, however, several factors that may interfere with the observation of grain boundary diffusion. The lateral diffusion between the boundary and the adjacent crystals may cause the penetration to be almost uniform across an advancing front, even when there is a rather large difference between the inter- and intragranular rates. This factor may practically obliterate any effects which might be found by the first method mentioned above, but it cannot interfere seriously with the sensitivity of the statistical (second) method.

Recrystallization or grain growth accompanying diffusion may cause the locations of the grain boundaries to shift and thus interfere with the first experimental procedure, but not seriously with the second.

Impurities of limited solubility are very likely to accumulate at grain boundaries. It is well known that the diffusion rate in a binary system may be greatly affected by the addition of a third substance, and that relatively insoluble materials may have a very pronounced influence. Thus impurities are likely to have a relatively larger effect upon intergranular diffusion than upon the overall rate.

It is possible too that the rate of condensation and absorption of a solute at the entrance surface of a grain boundary may be different from that at a crystal surface.

The indicator of the depth of penetration may give a false impression of the progress of intragranular diffusion, particularly when the appearance of a precipitate is being employed for this purpose, because precipitates are apt to form preferentially at the grain boundaries. Etches, also, frequently behave differently in the neighborhood of a grain boundary.

From these considerations it appears that the second method,

that of measuring the rate of diffusion in materials of different grain sizes, is likely to give the most trustworthy indication of the presence of grain boundary diffusion. Microscopic evidence of intergranular diffusion along a single grain boundary, whether positive or negative, should be admitted only with reservations.

Perhaps the most comprehensive study of intergranular diffusion yet conducted is that of the case of the diffusion of thorium into tungsten investigated by I. Langmuir (10) and his associates, by P. Clausing (11), and by G. R. Fonda, A. H. Young, and A. Walker (12). A comparison of the rates of dispersion of thorium into single crystalline and polycrystalline tungsten wires showed the rate to be much faster in the polycrystalline material. The difference decreased with rising temperature, and an extrapolation of the values reported (Fig. 10) seems to indicate that the rates for inter- and intracrystalline diffusion would become identical at an infinite temperature (reciprocal of the absolute temperature equal to zero).

Similar studies conducted by J. A. M. van Liempt (13) in the molybdenum-tungsten system and by C. Zwikker (14) in the carbon-tungsten system have demonstrated enormously greater diffusion along grain boundaries. It is interesting that much larger differences between the inter- and intragranular diffusion were observed in the systems involving the highly refractory metal tungsten than have been found among the lower melting metals. W. Seith and A. Keil (15), for example, were able to detect no influence whatever of the grain size upon the self diffusion of lead.

C. F. Elam (9) reported that zinc will not diffuse into a single crystal of copper until it has been distorted, and G. Edmunds (1) failed to observe any diffusion of copper into single crystals of zinc, although copper diffuses rapidly into polycrystalline zinc. In the present work, there has been experienced no difficulty in causing the diffusion of zinc and copper into annealed single crystals of copper and zinc respectively, but it has been found that the rate is much slower than that of the diffusion in the polycrystalline metals. In a single experiment in which thin copper electroplates were permitted to become absorbed by a single crystal of zinc and by a piece of cast polycrystalline zinc at 215 degrees Cent. (420 degrees Fahr.), it was observed that the copper color vanished in about one-sixth of the time in the polycrystalline sample. Precautions were taken to insure a uniform initial thickness of copper on the two specimens.

Despite the observation of a more rapid rate of diffusion in dis-

torted copper crystals, C. F. Elam could obtain no microscopic evidence of a more rapid penetration of zinc along grain boundaries. This may have been a result of recrystallization and grain growth during diffusion. There was no evidence of a more rapid diffusion

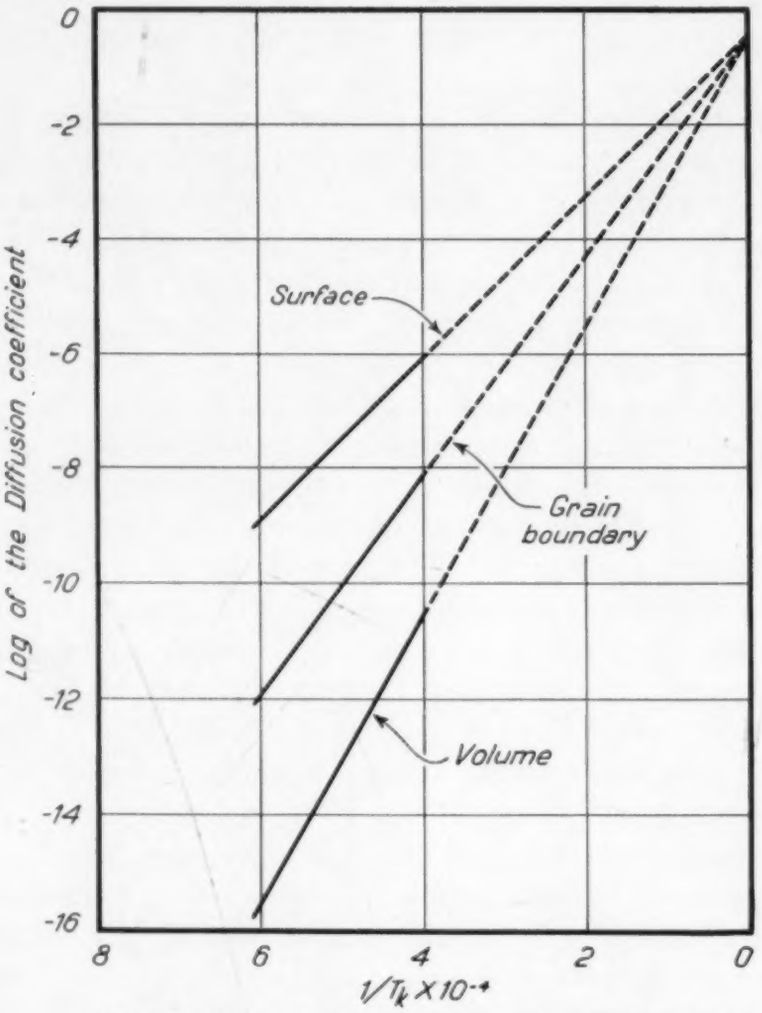


Fig. 10—Rate of Change of Diffusion Coefficient with Temperature for Thorium Diffusing Across a Tungsten Surface, Along a Grain Boundary, and Through the Body of a Tungsten Crystal. The Dashed Portions of the Curves Are Extrapolated and Appear to Meet at an Infinite Temperature.

along grain boundaries in the samples of Figs. 2 and 3, which were known to have suffered grain growth. The absence of microscopic evidence of intergranular diffusion in systems in which it might be expected to be found is common. For example, C. S. Smith's (16) micrographs of copper-silicon alloys, in which a band of SiO_2 was precipitated by inwardly diffusing oxygen, show no irregularity in the front of penetration of the oxygen.

There seems to be a widespread belief that in the iron-carbon system the carbon diffuses less rapidly in fine than in coarse-grained materials. D. H. Rowland and C. Upthegrove (2) in the course of a study of decarburization obtained results that seemed to confirm this view. The present authors, pursuing similar studies, have arrived at the conclusion that there is a very small effect in the opposite direction.

The method used by D. H. Rowland and C. Upthegrove consisted in the decarburization of commercial purity steels, similar except for their grain size, in suitable gas atmospheres at a series of temperatures above and below the transformation range. After cooling, the distribution of the carbon was determined from the microstructure and by chemical analysis. The microstructure in each case showed at the outside surface of the sample a band of ferrite that was sharply limited at its inside edge by patches of pearlite. In the photographs presented it may be observed that a steel having a number one grain size (16 grains per square millimeter) exhibited a wider band of ferrite than did a steel of a number seven grain size (1024 grains per square millimeter), but the difference between the ferrite band widths accompanying a number one grain size and those accompanying a number six grain size (512 grains per square millimeter) were much less than those between a number six and a number seven grain size. Thus, it appears that there may have existed some factor that was exerting a more powerful influence upon the diffusion rate than was the grain size.

The present work indicates that there may have been two quite distinct interfering factors operating in this case to mask the influence of the grain boundaries. In the first place, it is quite possible that there may have been a difference in the distribution of the impurities in the various steels used, and in the second place, it is almost certain that the samples suffered a redistribution of the carbon during the period of cooling from the diffusion temperature.

If the differences in the observed rates of diffusion were being induced by some unidentified variable such as the distribution of the impurities in the steel, it should be possible to avoid this difficulty by studying decarburization in samples taken from the same piece of steel and in which different grain sizes had been developed. This has been done, using a steel very similar in composition to one of those employed by D. H. Rowland and C. Upthegrove. In order to develop a large grain size, one sample was heated to 1125 degrees Cent. (2055

degrees Fahr.) for a half hour in a dry hydrogen[2] atmosphere, after which it was cooled to 925 degrees Cent. (1700 degrees Fahr.), the diffusion temperature. The second sample was then introduced into the furnace and both were held at 925 degrees Cent. (1700 degrees Fahr.) for 24 hours in moist hydrogen. One set of samples treated in this way was allowed to cool to room temperature in the furnace, while another was quenched. Upon examination of the slowly cooled samples, it was found that the ferrite bands in the coarse and fine-grained materials were of almost identical thicknesses. Slight irregularities in the boundaries of the ferrite zones made it difficult to detect visually small differences in the band widths, but by measuring the widths in a hundred places selected at random a set of average values was obtained which revealed a slightly greater width of the band in the fine-grained specimens. These average values were 0.0145 inch for the coarse-grained samples and 0.0150 inch for the fine-grained samples. Thus, a very slightly faster rate of diffusion along grain boundaries than across the grains was indicated.

As further proof of this point, similar experiments have been carried out using a high purity iron alloy containing 1 per cent carbon and 0.15 per cent aluminum oxide[3] (Al_2O_3). It was necessary to use an alloy with Al_2O_3 in order to retain a fine grain size (number 4, 128 grains per square millimeter) at the diffusion temperature. The large grain size (number -3 to 1, 1 to 16 grains per square millimeter) sample was produced by heating at 1050 degrees Cent. (1920 degrees Fahr.) for 1 hour in argon and then cooling to the diffusion temperature of 910 degrees Cent. (1670 degrees Fahr.). After a 2-hour treatment at 910 degrees Cent. (1670 degrees Fahr.) in a hydrogen-water vapor mixture, some of the samples were quenched and others cooled at a rate of 5 degrees Cent. per minute. The structures of typical slowly cooled specimens are shown in Figs. 11a (coarse grain size) and 12a (finer grain size). There is little, if any, difference in the widths of the ferrite bands in these two cases, but the total amount of massive ferrite visible in Fig. 12a is greater than that in Fig. 11a. At higher magnification, however, (Fig. 11c) there was observed a considerable amount of proeutectoid ferrite in the pearlite of the coarse-grained steel. It may be that the

[2]It is known that the rate of decarburization in dry hydrogen is much lower than in wet hydrogen. In fact, according to C. R. Austin (19) the amount of decarburization that occurs in pure dry hydrogen is negligible.

[3]Steels employed by G Derge, A. R. Kommel, and R. F. Mehl, TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 153, were used for this purpose.

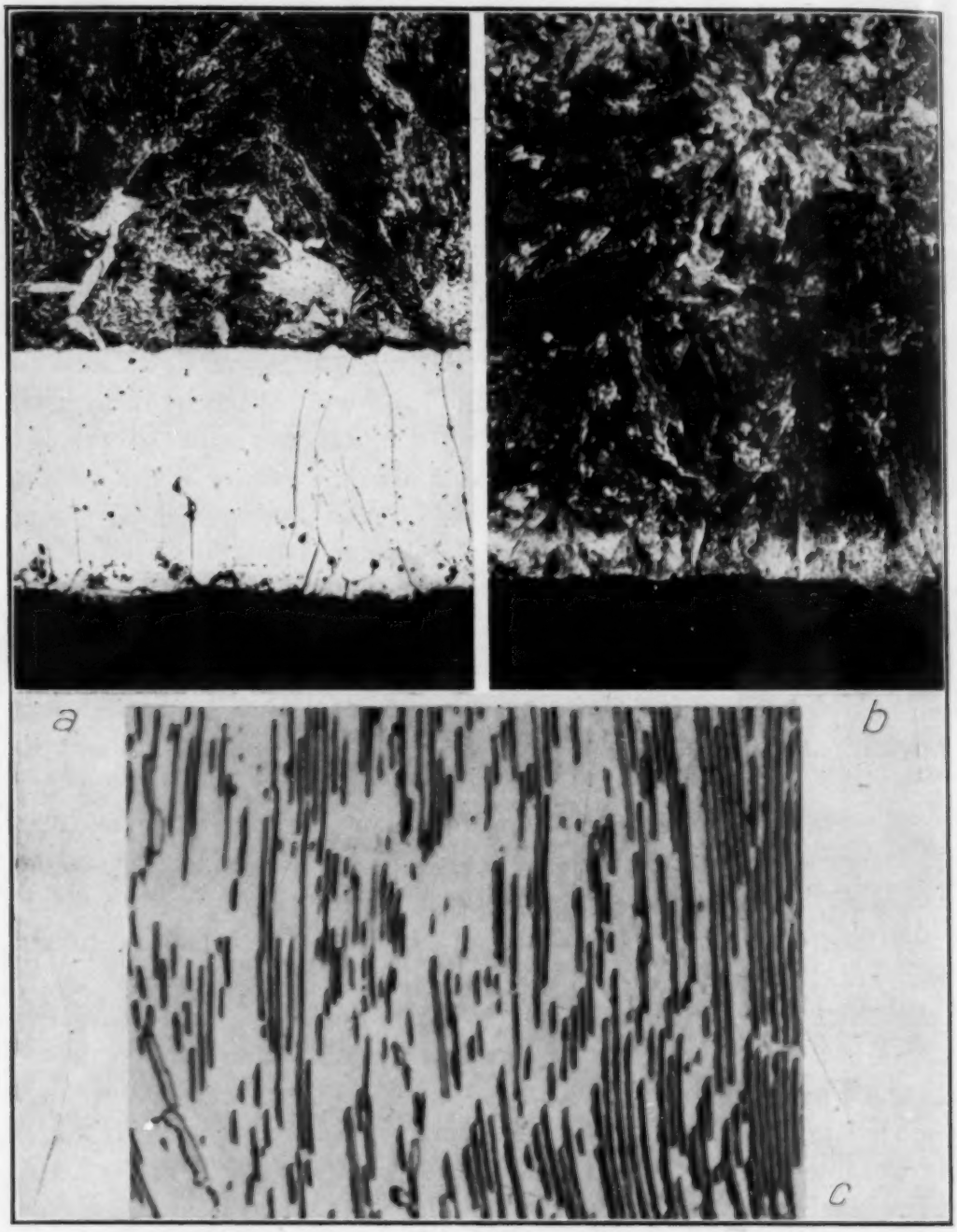


Fig. 11a—Coarse-grained Iron Containing 1 Per Cent Carbon and 0.15 Per Cent Al_2O_3, Heated to 1050 Degrees Cent. for 1 Hour in Argon to Develop a Number —3 to 1 Grain Size (1 to 16 Grains Per Square Millimeter), Cooled to 910 Degrees Cent., Decarburized 2 Hours in Hydrogen-Water Vapor Mixture, and Cooled to Room Temperature at a Rate of 5 Degrees Cent. Per Minute. White Band Is Ferrite and Dark Mainly Pearlite. Nital Etch. × 100.

Fig. 11b—Same as Fig. 11a Except that Sample was Quenched from Decarburizing Temperature. Shows Approximate Distribution of Carbon at Decarburizing Temperature and Indicates that a Marked Redistribution of Carbon Took Place During Slow Cooling, Fig. 11a. Nital Etch. × 100.

Fig. 11c—A Detail of the Pearlite Zone of Fig. 11a Just Above the Ferrite Zone. This Shows that the Structure Which Appears to be Pearlite in Fig. 11a is Actually Hypoeutectoid. Nital Etch. × 2000.

total proeutectoid ferrite present in comparable areas of the two steels was identical. As before, then, the difference in the diffusion rates has been either negligible or in the direction of a faster rate in the fine-grained material. Lest it be objected that some decarburization might have occurred during the growth of the coarse-grained structure, it should be pointed out that this could lead only to an increase in the width of the ferrite band in the coarse-grained sample, whereas the opposite effect was observed.

A separate experiment has been conducted to show that the Al_2O_3 present in these alloys did not significantly affect the results obtained. Two samples, both of a number one grain size (16 grains per square millimeter), one containing about 1.0 per cent carbon and 0.15 per cent Al_2O_3 and the other about 1.0 per cent carbon with no Al_2O_3 were decarburized at 910 degrees Cent. (1670 degrees Fahr.) for 2 hours and cooled at a rate of 5 degrees Cent. per minute. Within the limits of the error of measurement under the microscope, the ferrite bands were of the same width in the two samples, and the microstructures appeared to be identical in all respects.

The rates of diffusion in carburization and decarburization should be similar with respect to their dependence upon the microstructure. A high purity steel containing 0.1 per cent carbon and 0.15 per cent Al_2O_3 was treated to produce a variety of grain sizes and was carburized at 920 degrees Cent. (1690 degrees Fahr.) for 2 hours in a hydrogen-dipentene-benzene mixture. Coarse-grained (number -3, 1 grain per square millimeter) material was made by heating to 1100 degrees Cent. (2010 degrees Fahr.) for 1 hour in argon and then cooling to the diffusion temperature. Other samples heated directly to the diffusion temperature retained a number six grain size (512 grains per square millimeter). The relative depths of carbon penetration are shown in Figs. 13, 14, 15, and 16. Although the carbide zone appears a little wider in the fine- than in the coarse-grained alloy, the difference is too small to allow the conclusion that diffusion has proceeded more rapidly in the fine-grained sample. A difference in the ease of nucleation of the ferrite in the two cases might cause a difference of this magnitude.

The second factor mentioned above as having an influence upon the experimental observation of decarburization is the redistribution of carbon during the period of cooling from a temperature between A_4 and A_3. That such a redistribution does take place is clearly demonstrated by a comparison of the decarburized samples that were

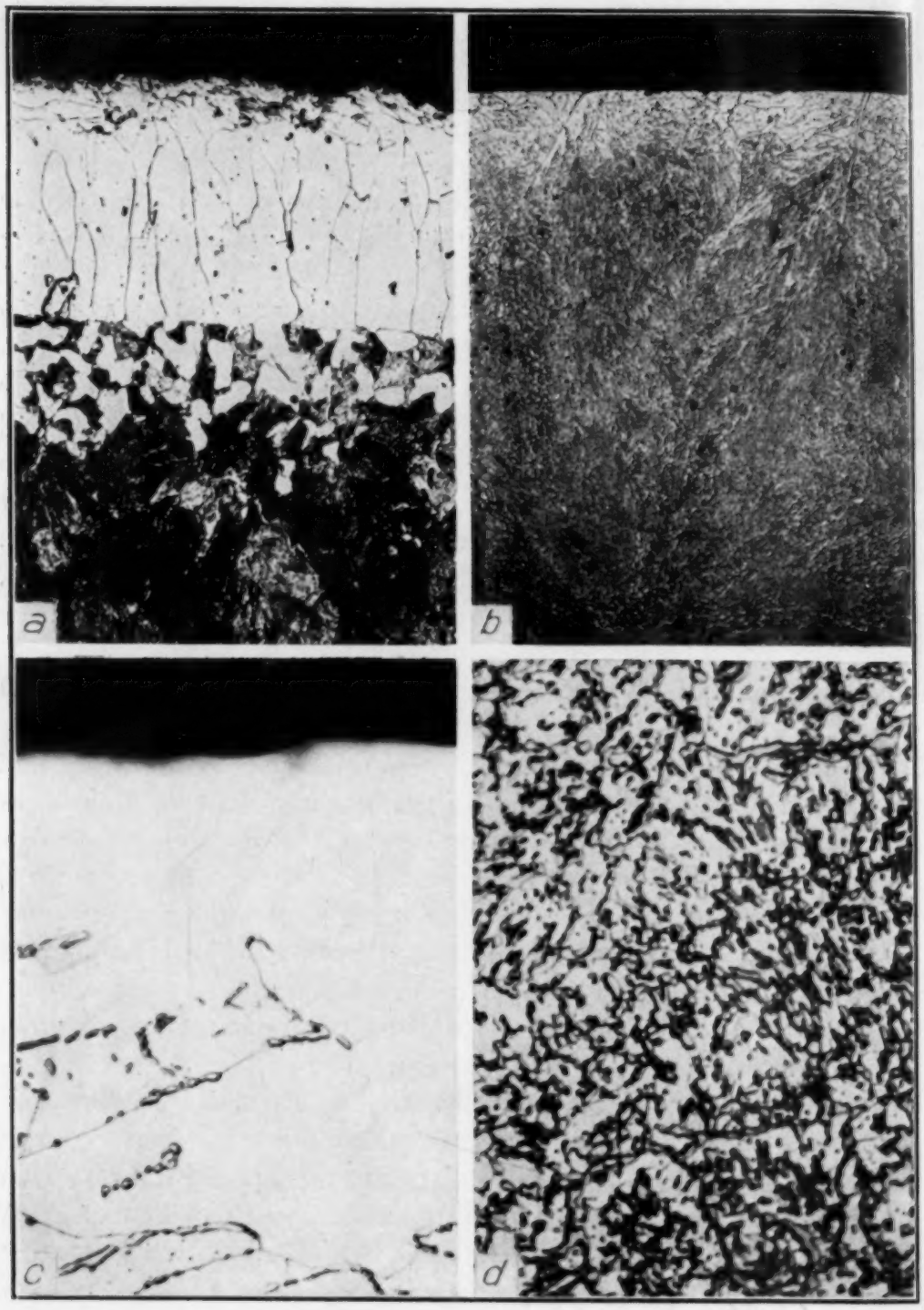


Fig. 12a—Fine-grained Iron (Number 4 Grain Size, 128 Grains Per Square Millimeter) Containing 1 Per Cent Carbon and 0.15 Per Cent Al_2O_3, Decarburized by Heating for 2 Hours at 910 Degrees Cent. in a Hydrogen-Water Vapor Mixture and Cooled at a Rate of 5 Degrees Cent. Per Minute. White Phase is Ferrite, and Dark Structure Pearlite. Compare Ferrite Band with Fig. 11a. Nital. × 100.

Fig. 12b—Same as Fig. 12a Except Quenched from Decarburizing Temperature and then Tempered for 15 Minutes at 600 Degrees Cent. and Quenched Again. Shows the Distribution of the Carbon at the Decarburizing Temperature. Nital Etch. × 100.

Fig. 12c—Detail of Fig. 12b Near Outside Surface. Nital Etch. × 1500.

Fig. 12d—Detail of Fig. 12b Near Center Showing the Higher Concentration of Carbon in This Region. Nital Etch. × 1500.

slowly cooled with those that were quenched from the diffusion temperature (Figs. 11a, 11b, 12a, and 12b). When the quenched samples were subsequently tempered, it became evident that there was nowhere a sudden increase in the carbon concentration corresponding to that occurring at the limit of the ferrite band in the slowly cooled

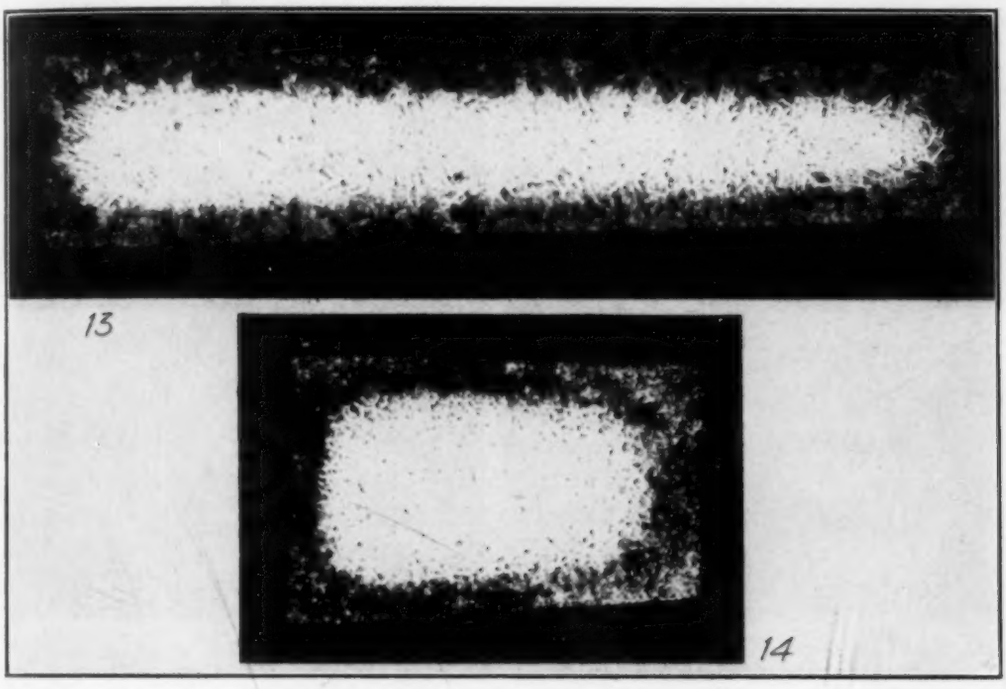


Fig. 13—Coarse-grained Iron Containing 0.1 Per Cent Carbon and 0.15 Per Cent Al_2O_3 Heated to 1100 Degrees Cent. for 1 Hour in Argon to Develop a Number −3 Grain Size (1 Grain Per Square Millimeter), Cooled to 920 Degrees Cent., and Carburized for 2 Hours in a Hydrogen-Dipentene-Benzene Atmosphere, and Cooled to Room Temperature at a Rate of 5 Degrees Cent. Per Minute. Dark Band Indicates Approximate Depth of Carbon Penetration. Nital Etch. × 10.

Fig. 14—Fine-grained Iron Identical with that Shown in Fig. 13 but Having a Number 6 Grain Size (512 Grains Per Square Millimeter), Heated Directly to 920 Degrees Cent. and Carburized for 2 Hours Before Cooling at a Rate of 5 Degrees Cent. Per Minute. Nital Etch. × 10.

samples. The details of the structure of the tempered sample of Fig. 12b are shown in Figs. 12c and 12d.

Evidently the explanation of this behavior requires a mechanism of transformation that will induce a rapid diffusion of carbon away from the surface zone during the cooling period. The phase diagram of the iron-carbon system shows that the transformation will begin in the metal which is lowest in carbon, in the case of decarburization the surface of the samples. Since the solubility of carbon in ferrite is very low in the higher temperature range, some carbon may be rejected to the adjoining γ crystals. If the cooling is sufficiently slow, additional quantities of ferrite will grow upon these first crystals

with a further rejection of carbon toward the inside of the sample. As the temperature of transformation approaches the A_1 the solubility of carbon in the ferrite increases slightly. At the core the austenite, still containing about 1.0 per cent of carbon, will become supersaturated, and a small amount of cementite will be precipitated.

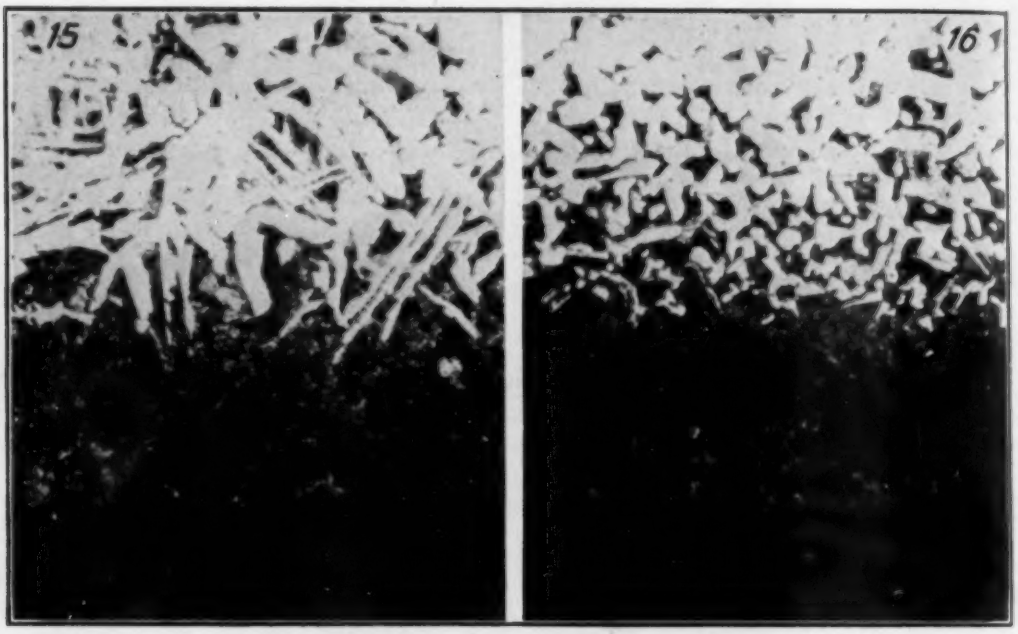


Fig. 15—Same as Fig. 13, but Taken at a Magnification of × 50.
Fig. 16—Same as Fig. 14, but Taken at a Magnification of × 50.

Finally at the A_1 temperature the balance of the γ phase, now fully enclosed in a shell of α, transforms to α plus Fe_3C in a eutectoid reaction. The carbon distribution that should be expected to result from such a mechanism is illustrated by the dotted curve of Fig. 17. Upon further slow cooling below the A_1 temperature it is probable that the peak in the carbon concentration at the limit of the ferrite band would be dispersed, and that a smooth curve showing a more or less abrupt rise at the limit of the ferrite band would result. Very rapid cooling from above the A_3 temperature may be expected to so shorten the time for diffusion that the redistribution of the carbon would be negligible.

In cooling from diffusion temperatures below the A_1 no such behavior could be expected, but within the A_1-A_3 range, where a band of ferrite may be formed upon the austenite base at the diffusion temperature, it seems probable that a widening of the ferrite zone would occur during slow cooling. The structure of a sample

decarburized in this range and quenched is shown in Fig. 19. The type of carbon distribution to be expected at diffusion temperatures above the A_3 and below A_1 is illustrated in the solid line curve of Fig. 17, while the probable form of the curve at the intermediate temperature is given in Fig. 18.

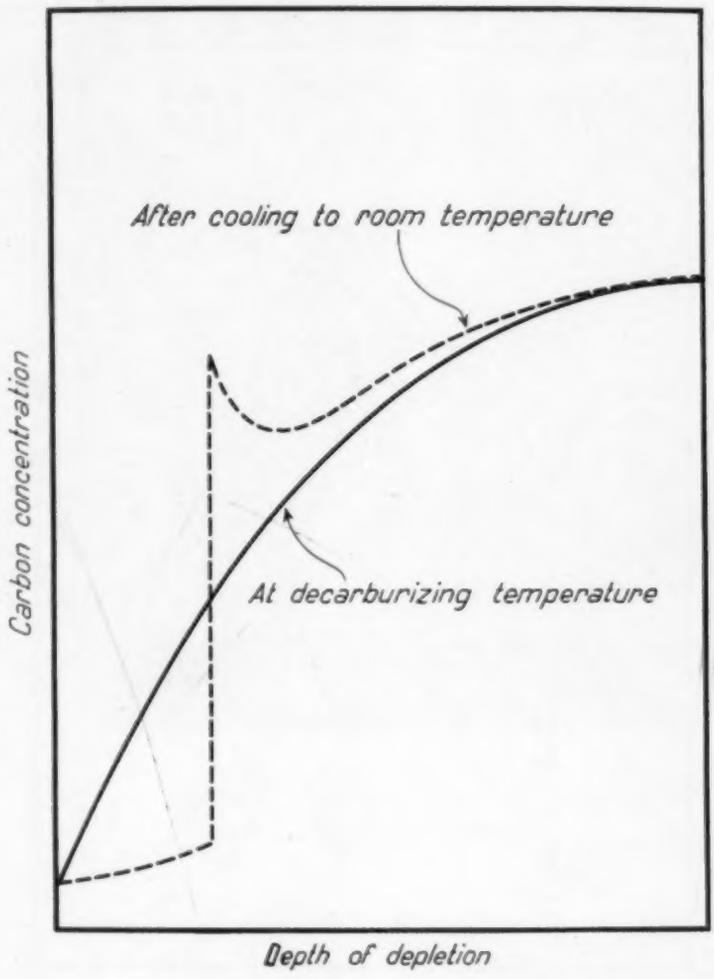


Fig. 17—Ideal Depth-Concentration Curves for Cases of (1) Carbon Distribution at a Decarburization Temperature Above A_2 or Below A_1, and (2) Carbon Distribution at Room Temperature in a Sample Decarburized Above the A_3 Temperature and Slowly Cooled Through the A_3-A_1 Range.

As it is generally recognized that the γ to α transformation proceeds more rapidly in fine- than in coarse-grained steels, it may be that the width of the ferrite band produced by slowly cooling a steel from a decarburizing temperature above the A_3 may be controlled to some extent by the grain size. That the grain boundaries can play an important part in the transformation process is thor-

oughly established and is illustrated again by the abnormal structure in the pearlite zone of Fig. 19. The abnormality in this instance can hardly be assigned to the presence of oxygen, in view of the long treatment of the sample in a hydrogen atmosphere.

Thus, the ferrite band widths observed by D. H. Rowland and C. Upthegrove may have been a measure of the carbon redistribution

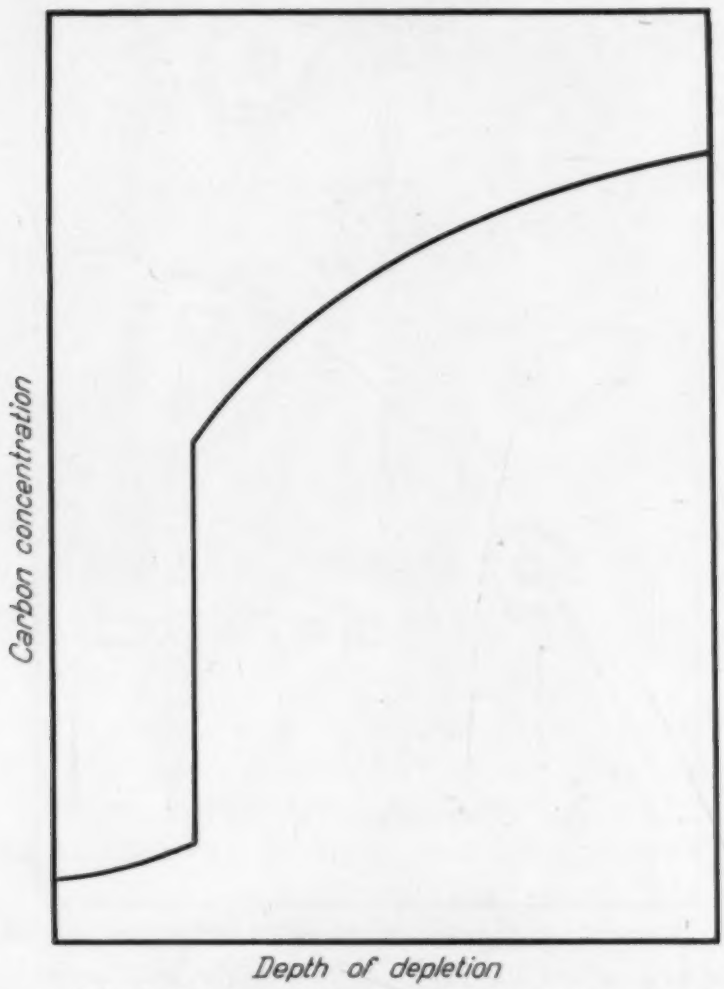


Fig. 18—Ideal Depth-Concentration Curve for a Sample Decarburized at a Temperature Between A_1 and A_3.

and of the influence of the grain size upon the carbon redistribution rather than of the total quantity of carbon extracted during the decarburizing treatment. If this is true, it follows that the observation of a greater ferrite band width in the coarse-grained steels may not in this case be taken as proof of a faster rate of intra- than of intercrystalline diffusion.

In the course of a brief study of the diffusion of nitrogen into

iron micrographic evidence has been obtained of a slightly faster rate of advance along α-phase grain boundaries. Two samples of high purity iron, one having a number -3 grain size (1 grain per square millimeter) and the other a number five grain size (256 grains per square millimeter) were nitrided in a partially dissociated ammonia

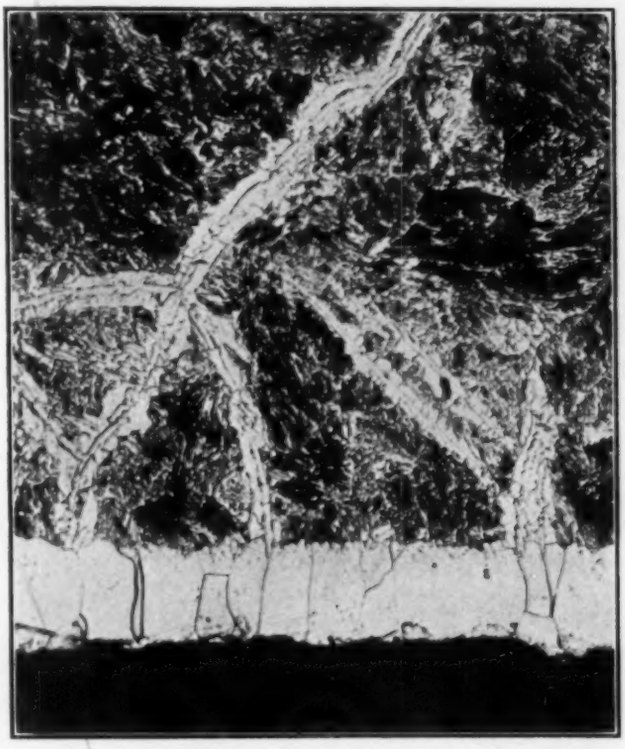


Fig. 19—Iron-Carbon (1.3 Per Cent Carbon) Alloy Decarburized in a Hydrogen-Water Vapor Mixture for 8 Hours at 750 Degrees Cent. and Quenched. Shows the Ferrite Band Formed Upon Decarburizing at a Temperature Between the A_1 and the A_3. Nital Etch. × 100.

atmosphere for thirty hours at 525 degrees Cent. (980 degrees Fahr.), at the end of which period they were slowly cooled. The microstructures (Figs. 20 and 21) show the precipitation of the iron nitride phase to a somewhat greater depth in the fine-grained alloy. This observation is, of course, subject to the possible influence of the grain boundaries upon the nucleation of the precipitate.

Except in the case of the diffusion of copper into zinc mentioned above, no evidence of a more rapid inter- or intragranular diffusion has been found among the copper-zinc alloys, possibly because of the grain growth that accompanies diffusion in that system. In several 70-30 brass samples that were subjected to dezincification in a vacuum

at 775 degrees Cent. (1425 degrees Fahr.), zinc was lost more rapidly at the intersections of the grain boundaries with the outside surfaces (Fig. 22a). This behavior cannot be accepted as proof of faster intergranular diffusion, however, because the grain boundaries were

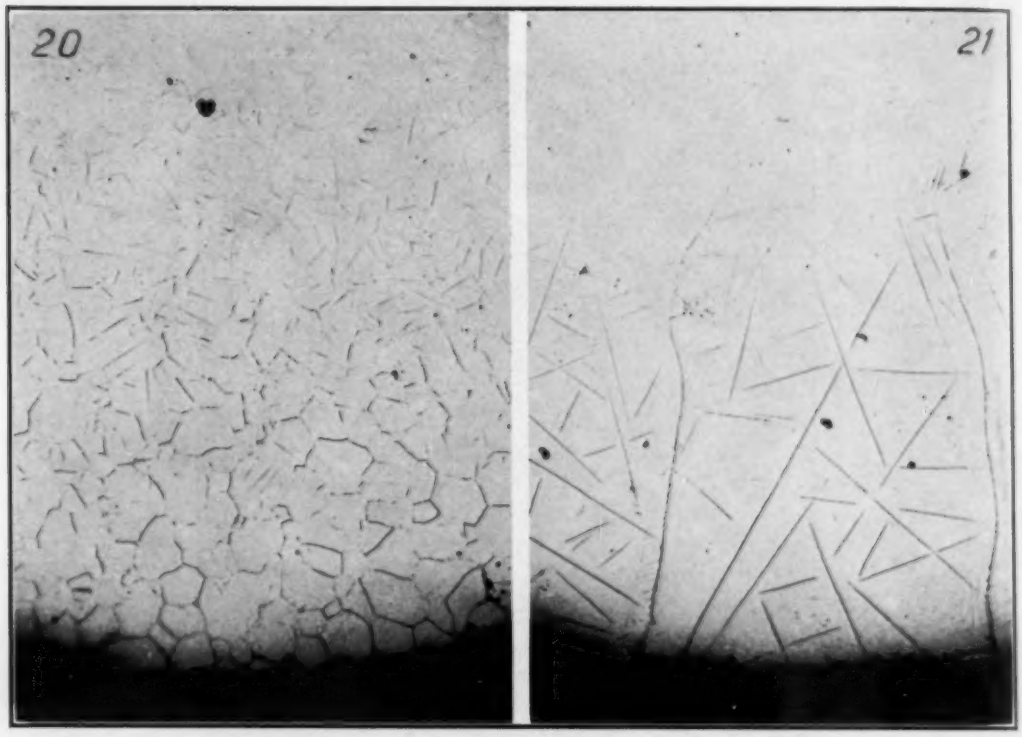


Fig. 20—Fine-grained α Iron (Grain Size Number 5, 256 Grains Per Square Millimeter) Nitrided in an Ammonia Atmosphere for 30 Hours at 525 Degrees Cent. and Cooled at 10 Degrees Cent. Per Minute. Compare the Depth of Occurrence of the Nitride Precipitate with that in Fig. 21. Picric Acid Etch. × 60.

Fig. 21—Coarse-grained α Iron (Grain Size Number −3, 1 Grain Per Square Millimeter) Nitrided in the Same Manner as the Sample of Fig. 20. Picric Acid Etch. × 60.

found to have opened into cracks (Fig. 22b) through which the zinc vapor could readily escape. It is well known that evaporation takes place more rapidly at grain boundaries even in pure metals, and this effect together with the large volume shrinkage that accompanies the loss of zinc from brass could account for this behavior as well as could intergranular diffusion.

Summary

1. The changes in microstructure accompanying diffusion have been discussed. Columnar grain formation occurs in systems involving a phase change. Recrystallization, grain growth, and twinning have been found in the copper-zinc system, but not in single-

phase alloys of chromium and nitrogen with iron. It is concluded that recrystallization, grain growth, and twinning may be induced by diffusion, chiefly when relatively large specific volume changes are caused by the movement of the solute, that is, when the lattice

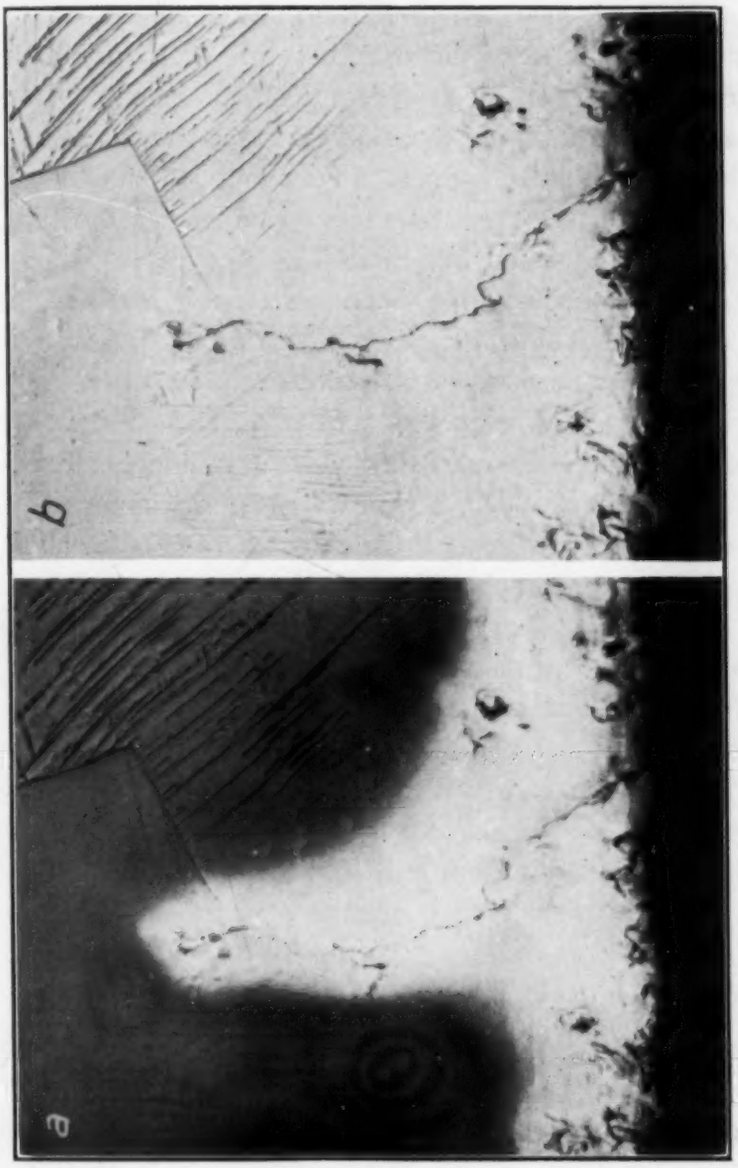


Fig. 22a—Zone of Dezincification at Grain Boundary in a Bicrystal of 70-30 Brass Heated to 790 Degrees Cent. for One Hour in a Continuously Pumped Vacuum. Etched with Ammonia and Hydrogen Peroxide Etch. × 75.
Fig. 22b—Same as Fig. 22a with the Etching Stain Removed to Show the Crack at the Grain Boundary.

parameter change is large and when the concentration gradient is steep. The shape of the specimen and the initial grain structure may also influence this recrystallization behavior.

2. Previous investigations of the anisotropy of diffusion have demonstrated the existence of large effects among the non-cubic

metals and one case of anisotropy in a cubic metal system. They have demonstrated also that the effect is temperature-sensitive and is dependent upon the concentration of the solute. The factors that may interfere with the observation of anisotropy have been discussed. New evidence for an anisotropy of diffusion in the copper-zinc system has been presented, in which system a marked dependence of the anisotropy upon the concentration of the solute was found. It has been pointed out that the largest anisotropic effects occur at the solute concentrations corresponding to the slowest rates of diffusion in the two cubic alloy systems in which directional effects have been observed.

3. In the metal systems in which the relative rates of intra- and intergranular diffusion have been previously studied, it has usually been found that intergranular diffusion is faster. In the tungsten-thorium alloys, the degree of intergranular diffusion varies with the temperature. The means available for studying intergranular diffusion have been discussed, and it is concluded that the methods involving a comparison of the rates of diffusion in coarse- and fine-grained metals are most to be trusted. Other investigators have concluded that, contrary to the behavior in other systems, the intergranular diffusion of carbon in iron is slower than the intragranular diffusion. The present investigation of the rates of the carburization and decarburization of iron and steel has shown a very slightly higher rate of intergranular diffusion. The disagreement between this and previous observations may have been caused by a dissimilar distribution of the impurities in the alloys of the previous investigations and by a redistribution of the carbon upon cooling from the diffusion temperature. New evidence of a possible faster rate of intergranular diffusion of nitrogen in iron and of copper in zinc has been presented.

Acknowledgments

The authors take pleasure in expressing their indebtedness to Dr. R. F. Miller for supplying the zinc single crystals, to Messrs. John G. Sullivan and Alfred Puglielli for contributing the results of their senior thesis researches, and to the members of the Metals Research Laboratory for their suggestions and assistance.

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DISCUSSION

Written Discussion: By E. P. Polushkin, consulting metallurgical engineer, New York City.

The authors have contributed new valuable data to our scant knowledge of the influence of microstructure upon diffusion in solid metals. This subject

has not been systematically investigated, and the present paper would undoubtedly stimulate interest in it.

The authors do not give an exact definition of the term "anisotropy of diffusion", but from the paper it is evident that they use it in a much broader sense than it is customarily used in crystallography. For example, in the description of their experiment with a piece of copper placed in brass chips, anisotropy of diffusion is interpreted as a difference in the rates of diffusion along different directions (or planes) in a single crystal, that is, in a true crystallographic sense. On the other hand, when the authors describe intergranular diffusion, they define this term as "difference in the rate of diffusion along grain boundaries and through the crystals of a polycrystalline metal" (page 640). There is no objection to the use of the term in a broad sense, but the latter definition does not imply any possibility of measuring the rates of diffusion, since the advance of a solute through the crystal of a solvent may go in many complicated ways. To substantiate this statement I shall refer to diffusion of corrosive liquids in metals. I had many occasions to examine corroded metals under the microscope, and, in my opinion, the dependence of diffusion upon the microstructure may be traced in these metals very well. In ancient copper and bronze which had been buried in the ground for long periods of time one can observe the processes of diffusion and corrosion operating concurrently, and the path of diffusion is well seen, for it is marked by deposition of the corrosion products. Of course, diffusion in those ancient objects was acting very slow and at ordinary soil temperatures, and for this reason the results may be different from those usually found in the laboratory specimens, but the essential features of the process of diffusion must be the same. The photomicrographs accompanying this discussion show different types of intragranular diffusion in corroded metals.

Fig. 1 shows an ancient bronze in which delta constituent has black color. The change from its normal white color to black was caused by penetration of a corrosive liquid through this constituent. Neither eutectoid nor proeutectoid alpha had been affected in any way, so that the structure remains otherwise unaltered. We see that in this case diffusion preceded the corrosion.

Fig. 2 shows a common type of corrosion in modern and ancient metals. Diffusion of a corrosive liquid had followed grain boundaries as well as cleavage planes within the grains. In other specimens, however, the cleavage planes resisted penetration of corrosion, and the mineralization of the metal was proceeding entirely from the grain boundaries.

In Fig. 3 is still another variation of intragranular diffusion. A corrosive agent was diffusing from grain boundaries into the body of grains in all directions at the same rate. As a result of this uniform penetration, the products of corrosion were deposited in concentric lines parallel to the boundary. A series of these lines are seen in each grain, while in the center of grains a small portion of the original metal can be found. These lines probably indicate a certain concentration of the corrosive liquid at which its reaction with the metal occurred.

Fig. 4 shows an irregular advance of diffusion through the grains, as indicated by the broken front line of the corrosion products. This is again a common case in old and modern metals.

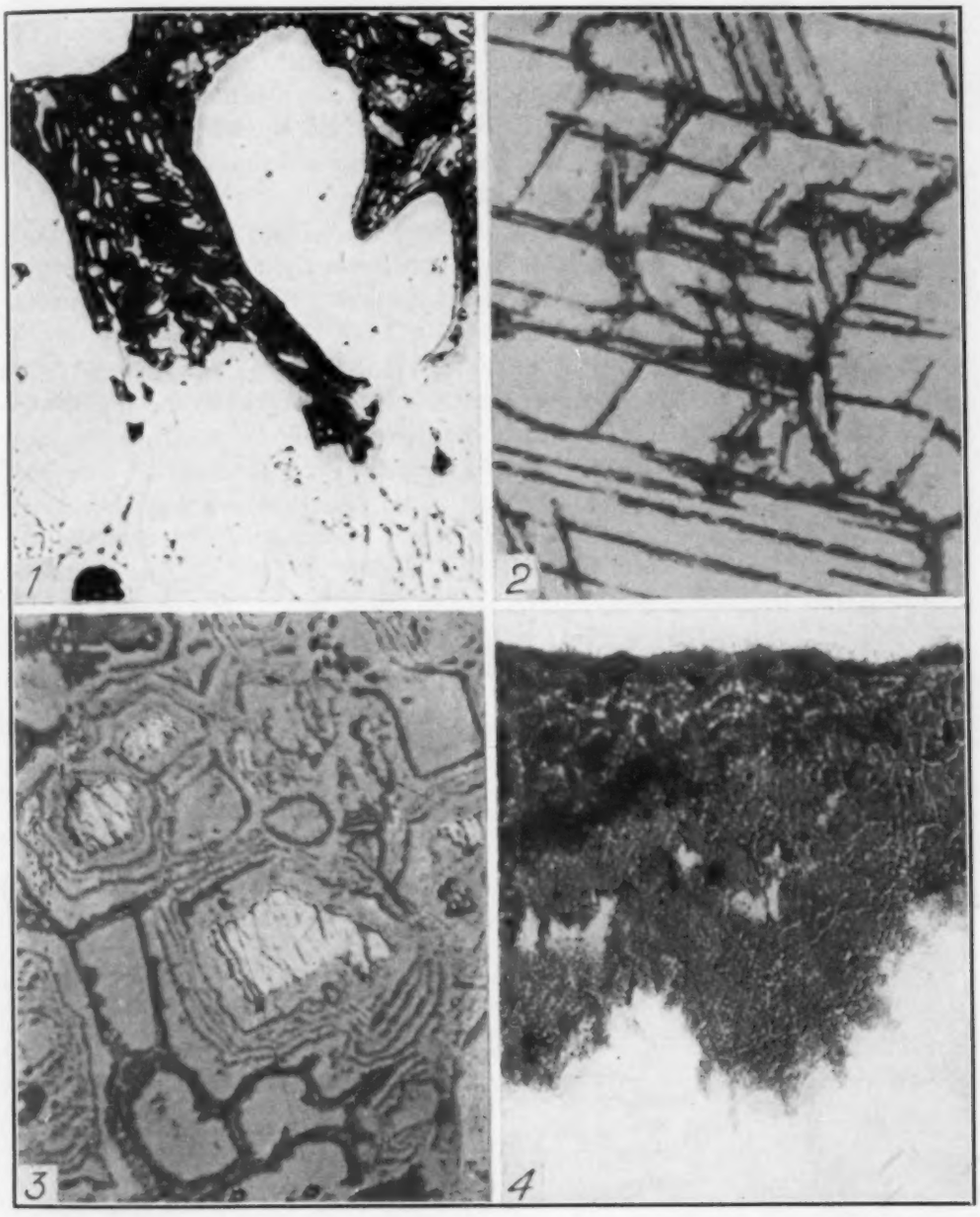


Fig. 1—Ancient Bronze. × 1000.
Fig. 2—Ancient Bronze. × 1000.
Fig. 3—Etruscan Bronze. × 1000.
Fig. 4—Etruscan Bronze. × 200.

The underlying cause of these variations is in the presence of impurities, in their specific nature and different distribution within the crystals. When we bear in mind all these variations, it seems very difficult to compare quantitatively the rates of diffusion along the boundaries and through the body of grains.

Written Discussion: By Floyd C. Kelley, Research Laboratory, General Electric Co., Schenectady, N. Y.

Diffusion of metals in the solid state has been of interest to the metallurgist since it was first observed. The structures resulting from diffusion as well as those influences which affect it have stirred the imaginations of many individ-

uals and aroused them to the point of investigation of this most fascinating phenomenon. Researchers in this field have contributed much to our knowledge, but there have been many conflicting ideas as to the mechanism and results of diffusion. In spite of the great advances made in the metallurgical field during the last quarter of a century this subject still remains a virgin field for investigation.

The complexity of the subject taxes not only our knowledge and imagination, but also our technique and for this reason we should take care to confine our investigations to the simplest forms to insure a firm foundation upon which to build.

The most outstanding contribution found in this paper is, to me, the observation of the great mobility of carbon in solid iron between the temperatures A_4 and A_3. The explanation by the authors accounting for the rejection of the carbon from the impoverished outer shell towards the carbon-rich core seems perfectly logical, and to my knowledge it is the first time that such an observation has been made. The authors are to be commended for bringing their observation as well as their interpretation to our attention at this convention.

Probably this observation has not been made before because one occupied with the heat treatment of steels would not normally quench a one per cent carbon steel from 910 degrees Cent. but rather from about 765 degrees Cent.

In the heat treatment of high carbon steels decarburization comparable with that revealed in this paper is probably rarely experienced, and when it is, the zone occupied by ferrite, as shown in this paper, is usually filled with iron oxide. One would not expect the diffusion of carbon to take place from a low carbon area to a higher carbon area.

The work of Rowland and Upthegrove on "Grain Size and Its Influence on Surface Decarburization of Steel" shows quite conclusively that the rate of diffusion of carbon is greater in coarse-grained steel than in fine-grained steel. The authors of this paper have shown that the opposite is the case, but I believe from the tone of their paper that they would not be too sure about it when their final judgment rests on the accuracy of many measurements and the difference between the measurements of the resulting ferrite zones amounts to only 0.0005 inch.

The experiments cannot be called duplicates for the data are obtained by using different diffusion times and temperatures, different steels, and different cooling rates.

When the photomicrographs of the quenched samples in these two papers are compared we find a marked difference. The quenching temperature used by Rowland and Upthegrove was 1410 degrees Fahr. while that used by the present authors was 1670 degrees Fahr. The steels used were of approximately the same carbon content but they were quenched from different temperatures.

The resulting photomicrographs in both papers probably give a true picture of the results to be obtained when treated as described.

If we assume that steel No. 9, Fig. 30 in the paper by Rowland and Upthegrove, and the steel represented in Fig. 11b in this paper are the same then we must conclude that the greater part of the carbon redistribution takes place between 1670 and 1410 degrees Fahr. The sample quenched from 1410

degrees Fahr. shows columnar ferrite while the sample quenched from 1670 degrees Fahr. reveals that the carbon is held in solution by the quench out to the very edge of the sample. If samples should be quenched at small temperature intervals from 1670 to 1410 degrees Fahr. one might expect to get a picture of the progress of this redistribution of carbon.

It would seem from their experiments that decarburization took place by carbon diffusing to the surface where it combined with oxygen and hydrogen. I wonder what the picture would have been if the sample had been decarburized for 50 hours instead of two before quenching.

The observation of an unexpected result serves best for tempering our judgment and for increasing our knowledge.

I wish to congratulate the authors on this very fine piece of work.

Oral Discussion

CLAIR UPTHEGROVE:[1] Messrs. Rhines and Wells are certainly to be complimented on their excellent paper on diffusion in metals. In discussing the paper I shall confine myself largely to that part dealing with intergranular diffusion, and with particular reference to the work of Rowland and Upthegrove on decarburization of steel.

In the work by Rowland and Upthegrove it was found that fine- and coarse-grained steels of substantially identical compositions do not decarburize alike and that under the same conditions the coarse-grained steels undergo the greater loss of carbon. The statement that the coarse-grained steels undergo the greater loss of carbon is of particular importance and though the statement as given above is quoted directly from the conclusions of the paper by Rowland and myself, it seems to have been missed at least partly by Rhines and Wells in the interpretation of the results.

On page 652 of their paper, they state that the ferrite bands observed by Rowland and Upthegrove may have been a measure of the carbon redistribution rather than of the total quantity of carbon extracted during the decarburizing treatment.

Reference to our paper will show that the width of the ferrite band was not used as the measure of the total carbon extracted or removed. The total carbon removed was obtained in each case by plotting the results of chemical analyses of cuts made at different depths, and taking the areas under the curves.

For comparative purposes, these values were expressed as carbon removed per unit of carbon originally present in the steel and formed the basis for the conclusions as previously stated and not, I believe, as interpreted by Rhines and Wells.

Further confirmation of the fact that in decarburization of fine- and coarse-grained steels of substantially identical composition the coarse-grained steels lose carbon to the greater extent or more rapidly than the fine-grained steels is shown in the results of tests recently made at 1600 degrees Fahr. in moist hydrogen, using samples $\frac{3}{16} \times \frac{1}{2} \times 4$ inches long of two steels, one fine-grained and the other coarse-grained, the fine-grained having a carbon content of 0.99

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[1]Professor of metallurgical engineering, University of Michigan, Ann Arbor, Mich.

per cent, manganese 0.40 per cent, the coarse-grained having a carbon content of 0.96 per cent, manganese 0.42 per cent.

The coarse-grained steels carrying 0.96 per cent carbon were completely decarburized at the end of 200 hours, while the fine-grained steels carrying 0.99 per cent carbon showed at the end of 200 hours a ferrite band of 0.0375 inch on each side and a band approximately 0.11 inch carrying carbon.

I believe this answers very definitely the question with regard to whether or not in the conclusions drawn by Rowland and Upthegrove we were dealing with the total amount of carbon removed, and shows that in this case the carbon in the coarse-grained steel was removed in a much shorter period than in the fine-grained steel.

The authors in referring to a possible carbon redistribution during the cooling through the A_3-A_1 range suggest a mechanism which will require a rapid diffusion of carbon away from the surface zone during the cooling period.

While the speaker is not ready to accept the proposed mechanism, we may, for the purpose of discussion, assume it to be workable. If the variations in the width of the ferrite bands of fine, and coarse-grained steels are then to be explained on this basis, that is diffusion away from a surface zone, must not the wider ferrite bands in the coarse-grained steels then be taken as evidence that the diffusion is more rapid in the coarse-grained steels than in the fine-grained steels?

Using a fine-grained steel of 0.76 per cent carbon, the authors have carried out a decarburization test at 1700 degrees Fahr. on samples of this steel in the fine-grained condition and also as coarsened after heating at 2050 degrees Fahr. The latter treatment produces a 1 to 3 grain size.

The results of these decarburization tests showed a ferrite band of 0.015 for the steel in the fine-grained condition as against 0.0145 inch in the coarse-grained condition or a variation of 0.0005.

Using a piece of the same steel the speaker coarsened one sample by again heating at 2050 degrees Fahr. and cooling to room temperature. This particular piece of steel was then checked as to the depth of decarburization and a $\frac{3}{16}$-inch layer removed from the round, which clearly took it well below any possible effect from the heating to the high temperature as regards decarburization.

This steel, with a sample of the same size as the steel in the fine-grained condition, was decarburized for 50 hours in moist hydrogen at 1310 degrees Fahr. This temperature was used for two reasons: first, that it eliminated the question of any possibility of carbon redistribution in cooling; second is that I delayed this somewhat and did not get around to find out just how Dr. Wells and Dr. Rhines brought about the entrance of their second specimen into the furnace with the first one after they had cooled from 2025 degrees Fahr.

Measurement of the ferrite bands showed a width of 0.0195 inch for the steel as coarsened as compared to 0.0175 inch for the fine-grained condition.

While a ready explanation for the differences shown here between our results and the results obtained by Dr. Wells and Dr. Rhines is not at hand, it appears reasonable that the method followed by the speaker was probably less subject to error than the method used by the authors.

Dr. Rhines and Dr. Wells have also made reference to the diffusion of copper in the zinc and in copper-zinc alloys with regard to the intragranular

and intergranular rates, and I believe I am correct in stating that with one exception they did not find any difference for the rates of diffusion, stating that possibly this was due to the fact that such processes in the copper-zinc alloys were usually accompanied by grain growth.

I should perhaps point out in connection with a possible redistribution of carbon during the cooling from the A_3 to A_1, that Rhines and Wells are basing their results on diffusion tests carried out above the A_3 of pure iron.

In the work of Rowland and Upthegrove most of the determinations were made at temperatures below the A_3 point, and consequently there was a phase change, gamma to alpha, readily possible during the decarburization.

Quenching experiments carried out on samples in the process of decarburization in this temperature range of the A_3 to the A_1 invariably showed the presence of ferrite bands.

I do not feel that the work of Dr. Rhines and Dr. Wells has presented sufficient evidence to justify the conclusion, particularly in the case of carbon steels, that the intergranular diffusion will always be the more rapid.

Authors' Reply

In view of the large number of self-consistent observations presented by Rowland and Upthegrove, the present authors are convinced that the observations and conclusions of these investigators are correct with respect to the commercial steels and the conditions of experiment employed. The present authors are likewise confident that their own, equally consistent, observations and conclusions concerning the effect of the grain size upon the diffusion of carbon in gamma iron are correct for high purity alloys treated at temperatures above the A_3. The cause of the apparent conflict in results probably lies in the composition of the steels studied and in the experimental conditions.

The presence of various impurities in the commercial steels used by Rowland and Upthegrove was mentioned in the paper as a possible cause of the difference in results, it being suggested that the kind and distribution of the impurities might account for the effects ascribed to the grain size. In this connection it is altogether possible that certain of the impurities tend to accumulate at the grain boundaries in such a manner as to delay the passage of carbon through those regions. It is well known both that third elements do have a pronounced influence upon the diffusion rate and that certain elements, notably those that form carbides, have a tendency to separate at the grain boundaries. Such an effect might very well prevent extensive grain boundary diffusion and produce the effects observed by Rowland and Upthegrove.

All of the experiments in the present paper dealing with intergranular diffusion were conducted with single phase alloys. This condition was chosen deliberately in order to avoid the complications which might arise from the occurrence of transformations during the diffusion tests. On the other hand, the experiments of Rowland and Upthegrove were carried out mainly at temperatures between A_1 and A_3 where the diffusion process is accompanied by a progressive transformation of gamma to alpha. They have thus introduced a number of factors which may or may not have influenced the final result. There is, first of all, a zone of transformation where alpha crystals are grow-

ing at the expense of gamma. The effect of grain size upon such a transformation is still too poorly understood to justify any extensive discussion of this point, but the fact that, during single phase recrystallization, large crystals grow at the expense of small crystals suggests that large alpha grains might grow more rapidly into gamma and thus provide an impetus to the diffusion process. Moreover, these experiments involve the diffusion of carbon through continuously growing alpha grains and through two phases where the rates of diffusion are undoubtedly different. Although the data at hand provide no means of positively identifying the influence of any of these variables in the observations of Rowland and Upthegrove, it remains possible that their influence was important.

Thus the present authors adhere to their opinion that the rate of the intergranular diffusion of carbon in gamma iron is either the same or slightly greater than the rate of intragranular diffusion. The observation of a contrary effect is probably to be ascribed to the influence of impurities or to the occurrence of a transformation or both.

There remain to be discussed several specific points raised by Professor Upthegrove. The point concerning the conclusions of Rowland and Upthegrove being based upon the total loss of carbon and not upon the microstructures is well taken, for a redistribution of the carbon could scarcely affect the total carbon loss. A re-examination of their analytical data of Table III shows that not only is the effect in the same direction as that indicated by the photomicrographs, but it is quantitatively similar. Assuming the analytical error in their work to be near the usual 0.005 per cent carbon, it appears that there is no certain difference in the carbon loss between the steels of number 1 and number 6 grain sizes (steels 1 and 2 treated at 1450 degrees Fahr.) and that there is a very definite difference between the rate of carbon loss from these two and the steel of a number 7 grain size (steel number 3). The contention of the present authors that the results of Rowland and Upthegrove indicate the operation of some factor other than grain size upon the diffusion rates in their steels, therefore, remains valid. It does appear, however, that the influence of the redistribution of the carbon upon their micrographic observations has been negligible, possibly because this effect was held constant by always using the same cooling rate.

In the light of the above, the influence of the carbon redistribution upon the ferrite band width seems less significant, yet there can be no doubt that the band width is materially changed during slow cooling from the diffusion temperature. Professor Upthegrove suggests that the extent of the carbon redistribution may be controlled by the grain size through its influence upon the diffusion rate, and where intergranular diffusion is slow a large-grained material would suffer more back-diffusion of carbon. That seems reasonable. It is the feeling of the present authors, however, that the widening of the ferrite band is more likely to be limited in fine-grained steels by the appearance of zones of ferrite separating ahead of the growing band and so enclosing the zones of high-carbon austenite that further back-diffusion is difficult. The supercooling of coarse-grained steels is generally much easier than that of fine-grained steels, because the nuclei necessary to the transformation appear principally at the grain boundaries. Thus the mechanisms proposed by Professor

Upthegrove and the authors would reinforce each other if grain boundary diffusion is less rapid than transcrystalline diffusion and tend to cancel if the reverse is true. On the other hand, the effect of the grain size upon the back-diffusion may be almost negligible because of the steep gradients involved.

The authors are tempted to believe with Professor Upthegrove that the evidence of the very beautiful micrographs in the paper by Kirkendall, Tomassen, and Upthegrove is in favor of the existence of less rapid grain boundary diffusion. This is another instance of the observation of diffusion at an interface of phase transformation, however, and for reasons cited in the paper the authors distrust micrographic evidence of this sort. Such an effect as that observed could be produced by anything which could delay the transformation at a grain boundary, as, for example, the more rapid arrival of an interfering impurity or the interference of the adjacent α grain where the rate of growth might be decelerated by the less ordered state of the lattice at the grain interface.

Mr. Polushkin has objected to our use of the word "anisotropy" in a non-crystallographic sense. Any departure from the use of this word in its strictest meaning was unintentional.

The photomicrographs presented by Mr. Polushkin are extremely interesting. They illustrate several cases not mentioned in the present paper, and the authors wish to thank Mr. Polushkin for permitting their publication here. The case of the preferential penetration of a solute through one of two coexisting phases suggests a whole new field of study, and the penetration along slip lines in bronze provides excellent confirmation of the belief that the diffusion rate is high in regions of concentrated stress. In the interpretation of structures resulting from corrosive action care should be exercised to distinguish between cases where the metal remains sound and dense and those where it is ruptured by the corrosion products or mechanism.

Mr. Kelley's comments have been answered for the most part in connection with the reply to Professor Upthegrove's discussion. One point requires further explanation. The photomicrographs of Rowland and Upthegrove, Fig. 30, and the present paper, Fig. 11b, are not comparable because the former was diffused below the A_3 temperature where a ferrite band must have formed during the diffusion process, and the latter was diffused at a temperature above the A_3 where no ferrite could form. Thus the band width of the sample of Rowland and Upthegrove is made up of two parts, the ferrite formed during diffusion and the additional ferrite formed during cooling, while the band shown in Fig. 11b was formed entirely during the cooling period.

The authors wish to thank Mr. Kelley, Mr. Polushkin, and Professor Upthegrove for their interest and their stimulating discussions.

COLOR CARBON AND AGING

By Carl L. Shapiro

Abstract

Part I of this paper discusses the effect of thermal and mechanical treatment upon the size of the iron carbide particles by means of the color carbon test which is a colorimetric method of determining the relative size of the iron carbide particles. It presents a brief historical development of color carbon and then proves that "missing" and "excess" carbon are due to the variation in the size of the iron carbide particles.

The effects of aging upon the iron carbide particle size are also studied by the color carbon test which shows that aging after thermal or mechanical treatment results in an increase of coloration or carbide particle size. These findings indicate that aging in carbon steels should be attributed to carbon (carbide) and is a precipitation and agglomeration process. Furthermore, the color carbon test shows that the aging characteristics of a steel are influenced by its structural composition and the degree of mechanical deformation.

Part II describes the aging of the various aggregates formed in steel and presents the cause of aging in these aggregates after defining the different types of aggregates and aging. It reveals that the aging characteristics of the aggregates vary and that aging in general is controlled by: (1) the amount of retained austenite, (2) the amount of carbon dissolved in alpha iron, (3) the size of the iron-carbide particles, (4) time and temperature of tempering and (5) the degree of mechanical deformation remaining within or conferred upon the steel after the final heat treatment.

Part II also shows that martensite is structurally of two types, (1) the acicular and (2) the spheroidal. It further reveals that aging converts the acicular type of carbide structure to the spheroidal form.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. This paper was condensed in part (Part I) from a thesis "The Effect of Heat Treatment, Aging and Working upon the Condition of Carbon in Steel" submitted to the Harvard Engineering School, Harvard University, in partial fulfillment of the requirements for the degree of Doctor of Science in Physical Metallurgy, Cambridge, Mass., December 1933, and from the Carnegie Scholarship Memoirs, Iron and Steel Institute, 1936. The author, Carl L. Shapiro, a member of the Society, is a consulting engineer in Syracuse, N. Y. Manuscript received June 25, 1938.

Finally, the effects of thermal and mechanical treatment upon the nitrogen content of various chromium and nitrided steels were studied. The results show "excess" and "missing" nitrogen in hardened and tempered steels respectively. The cause of this variation in nitrogen content is explained on the basis of particle size as in color carbon.

The report concludes with the statement that many of the volumetric tests (colorimetric or titration) are only relative since they are influenced by the size of the dissolving particles and, consequently, create marked variations in the calculated percentages of the element present in the material.

Part I

Color Carbon

AT the turn of the twentieth century, the entire metallurgical world was deeply concerned with the subject of "color carbon" and especially "missing carbon." The importance of this subject may be gathered by presenting some of the metallurgists who wrote and contributed much research and discussion upon this subject in the volumes of the American Institute of Mining and Metallurgical Engineers, The Iron and Steel Institute of England and, especially, in the Metallographist. Some of the more outstanding metallurgists were Sir Roberts-Austen, Arnold, Campbell, Le Chatelier, Eggertz, Heyn, Hogg, Howe, Baron Juptner von Jonstoroff, Mathews, Osmond, Parker, Rosenbloom, Sauveur, Stead, and Werth.

These investigators showed that when iron or steel containing from 0.10 to 6.50 per cent carbon was quenched from above the thermal critical range in water and tested for combined carbon by the Eggertz colorimetric test, approximately fifty per cent of the carbon was missing. This carbon, which could not be determined volumetrically, was called "missing carbon."

Many theories were presented to account for missing carbon. The two which were ardently supported by the leading metallurgists of the day were (a) that missing carbon was volatilized as a hydrocarbon gas during the dissolving of the carbide particles in the diluted nitric acid during heating, and (b) that missing carbon did not exist as normal iron carbide of the empirical formula $(Fe_3C)x$.

These two theories were believed for thirty years until Whiteley showed that the percentage of carbon evolved as a hydrocarbon gas

during heating was the same in both the annealed and quenched condition. Moreover, Whiteley showed that when the hardened steel, which contained approximately fifty per cent missing carbon, was tempered by small temperature intervals below the thermal critical range, the amount of missing carbon gradually diminished and then showed an excess of carbon. This surplus of carbon he termed "excess carbon."

Inasmuch as this question of missing and excess carbon was never satisfactorily answered, it was suggested in 1930 by Professor Albert Sauveur that the writer determine the cause of missing and excess carbon. This investigation was concluded six years later with the aid of a Carnegie Research Grant of the Iron and Steel Institute of England.[1]

Procedure

A perusal of the literature showed that the Eggertz colorimetric test for combined carbon had many modifications since its origination in 1862. Essentially, at present, it consists of dissolving a standard weighed sample in a test tube containing a definite volume of cold diluted nitric acid (1.2 specific gravity). As soon as the ferrite of the steel is dissolved, the test tube containing the acid solution and carbide precipitates is heated in either a water or glycerine-water bath until the carbide particles are dissolved, cooled rapidly in running water, and compared volumetrically against a standard by any of the following methods: (a) Eggertz colorimetric comparison tubes, (b) mirror colorimeters, or (c) photo-electrically.

Since Parker[2] and Hogg[3] showed that the standard should be of the same chemical composition as the unknown, the standard used throughout this investigation was the annealed condition of the steel instead of permanent colored solutions such as $FeCl_3$, $CoCl_3$, $CuCl_2$, etc., in hydrochloric acid as is commonly used. The volumetric comparison between the standard and unknown was made by method (a) which consists of diluting the acid solution of the unknown to the intensity of the standard in Eggertz colorimetric comparison tubes of equal bore and thickness. The volume of dilution is converted into per cent carbon by multiplying the volume reading by a constant (per

[1]Shapiro, C. L., *Carnegie Scholarship Memoirs*, Iron and Steel Institute, 1936, Vol. 25, p. 141.

[2]Parker, J. S., *Chemical News*, 1880, Vol. 42, p. 80.

[3]Hogg, T. W., *Journal*, Iron and Steel Institute, 1896, No. II, p. 179.

cent carbon per cubic centimeter). This constant is obtained by dissolving the annealed steel (standard) in an equal volume of acid as the unknown, and diluting the acid solution, after heating and cooling, into a convenient multiple of the true carbon content which may be determined by any of the following methods:

(1) Direct combustion in oxygen with a gravimetric, volumetric or titration determination of the carbon dioxide formed.
(2) Decomposition of the sample in chromic acid solution and the determination of the carbon dioxide evolved.
(3) Separation of the iron and carbon by the action of copper potassium chloride solution and combustion of the carbon residue.

These methods yield the total amount of carbon in steel regardless of the prior structural condition of the material. Further details concerning the procedure and modifications of these tests may be procured from any standard analysis text.

Material

Since maximum amount of missing carbon was shown to occur in hardened steel containing from 0.70 to 1.25 per cent carbon,[4] this entire investigation was conducted upon two basic electric steels of the following composition:

	C	Mn	Si	P	S	Ni	Cr
Steel A	0.87	0.39	0.13	0.014	0.020	0.03	0.04
Steel B	1.19	0.33	0.17	0.011	0.014	0.04	0.03

Prior to any investigation, the material was normalized from 850 degrees Cent. (1560 degrees Fahr.) and subsequently annealed at 825 degrees Cent. (1515 degrees Fahr.). The annealed material of each steel was used as the standard throughout the study.

Prior to hardening, standard specimens (1x1x½ inch) were cut and scored in order to obtain small sections to analyze. All specimens were heated in a specially designed furnace (Fig. 1) to prevent decarburization. The hardened specimens were tempered 30 minutes at temperature in preheated furnaces.

The Effect of Heat Treatment Upon Color Carbon

Since it was previously shown that quenching from 1000 degrees Cent. (1830 degrees Fahr.) yielded maximum missing carbon,[1] all

[4] Sauveur, A., *Journal*, Iron and Steel Institute, 1896, No. II, p. 191.

specimens were hardened from this temperature in water. The hardened and tempered specimens were tested immediately or within two hours after heat treatment. The results obtained after hardening and tempering these steels are shown in Fig. 2.

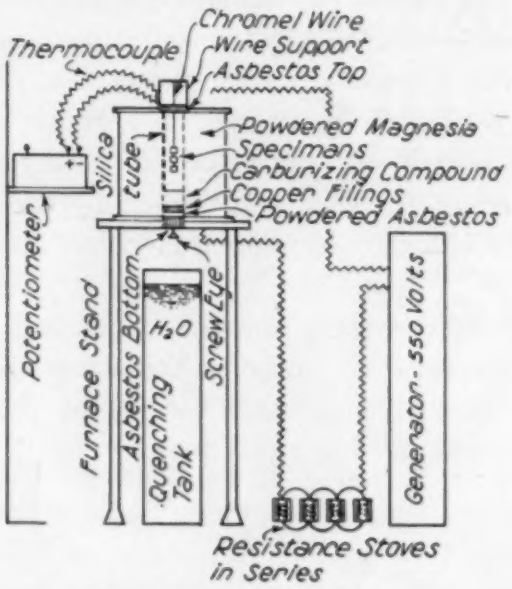


Fig. 1—Sketch of Vertical Quenching Furnace.

Fig. 2 shows that the apparent color carbon content increases from 0.42 to 1.11 per cent in Steel A and from 0.63 to 1.39 per cent in Steel B. This figure also shows that "missing carbon" becomes "excess carbon" at 550 degrees Cent. (1020 degrees Fahr.) in Steel A and at 500 degrees Cent. (930 degrees Fahr.) in Steel B. These temperatures may vary either way since a longer tempering period at a lower temperature or a shorter time at a higher temperature will affect the size of the iron carbide particles.

A study of the cold nitric acid solution and carbide precipitates in Steel A, obtained by dissolving the hardened and tempered specimens in cold diluted nitric acid (1.2 specific gravity), showed that three changes take place in the structure—form and color of the precipitates and acid solution. These changes occur in the temperature ranges extending from (a) the "as-quenched" condition to 250 degrees Cent. (480 degrees Fahr.), (b) 250 to 400 degrees Cent. (480 to 750 degrees Fahr.) and (c) 400 degrees Cent. (750 degrees Fahr.) to below the thermal critical range, and represent the martensitic, troostitic and sorbitic conditions in hardened and tempered steels.

The acid solution of range (a) is yellowish brown in color, and possesses a greenish cast which is covered with a frothy, white gelatinous substance. The carbide precipitates of this range are yellow and extremely fine. The acid solution of range (b) is light brown in color without any greenish cast and is covered with a thick brown

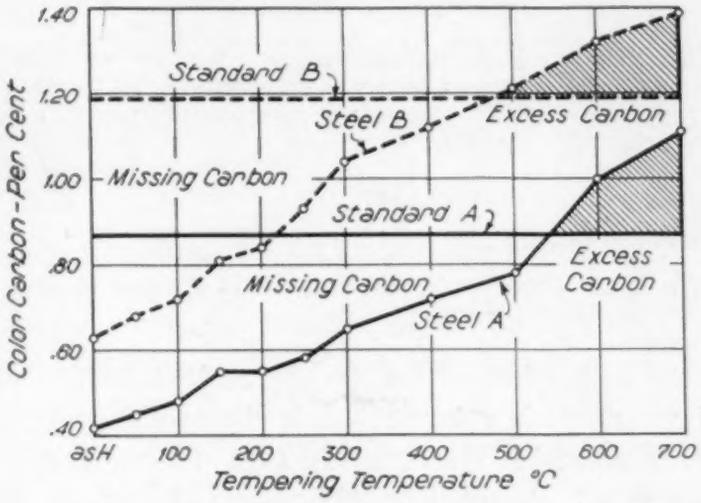


Fig. 2—The Effect of Tempering Upon the Color Carbon of Quenched Steels.

viscous substance. The carbide precipitates are flat, wide and irregular and possess a brownish, black appearance. The carbide precipitates of range (c) are round and black, and they become larger in size and fewer in number with the higher tempering temperatures. The acid solution of this range is colorless and does not contain any frothy or viscous substance.

To account for the loss of coloration (missing carbon) in quenched steel and the increase in tempered steels (excess carbon), the brown nitric acid solution obtained after heating was subjected to dialysis, charcoal filtration, filtration and dialysis and vice versa, dialysis and filtration. The results obtained by electro-endosmosis and filtration substantiate the work of Whiteley[5] and show that the brown nitric acid solution is colloidal in nature, structural in color, and divisible into three parts.

(a) A yellow-green solution which diffuses through the dialyzer (collodion bag) into the dialyzing medium (distilled water).
(b) A brown colored solution which remains in the dialyzer (collodion bag).
(c) A chocolate brown precipitate retained in the dialyzer.

[5]Whiteley, J., *Carnegie Scholarship Memoirs*, Iron and Steel Institute, 1917, Vol. 8, p. 1.

Since these conditions are caused by the difference in the size of the iron-carbide particles, they are explained empirically by Oswald and Fisher's diagram[6] in Fig. 3.

Coarse Dispersions	Colloids	Molecular Dispersoids
	Increase in degree of Dispersion →	
	0.1 μ* to 1.0 $\mu\mu$**	
Periods greater than 0.1 μ; do not pass through paper filters; microscopically analyzable.	Pass through paper filters; cannot be analyzed microscopically; do not diffuse or dialyze.	Periods smaller than 1.0 $\mu\mu$; pass through filter paper, cannot be analyzed microscopically; diffuse and dialyze.
(Phase C)	(Phase B)	(Phase A)

*μ = 0.0001 mm.
**$\mu\mu$ = 0.0000001 mm.

Fig. 3—Oswald and Fisher's Diagram of Dispersed Systems Showing the Effect of Particle Size Upon Filtration and Dialysis.

Since the coloration of the brown acid solution is colloidal in nature and structural in color and since the solubility of any solid in either a liquid or solid is a function of time, temperature and particle size (surface area), the state of division of the solute, for constant time and temperature, determines the rate of solution. Therefore, heat treatment determines the size of the iron carbide particles and ultimately controls (a) the rate of decomposition that occurs in nitric acid when the carbide particles are dissolved, (b) the coloration of the acid solution and (c) the rate of color decay. Consequently, when the standard (annealed steel) is dissolved in nitric acid and compared against an unknown, the variation in the particle size of the iron carbides creates a difference in the acid solubility and, as a result, the coloration of the acid solution varies directly from yellowish green to deep brown with the particle size. This colorimetric comparison of particle sizes creates missing and excess carbon and is pictured schematically to occur in the following diagram by allowing X to equal the carbide particle size of any standard steel.

"Missing Carbon" ← any particle size smaller than X **X** any particle size larger than X → "Excess Carbon"

If the particle size X of the hardened (quenched) steel were used as a standard instead of the annealed structure, there would be no missing carbon but only excess carbon, since the particle size would always be larger; whereas, if the large carbide condition which

[6]Oswald, W. and Fisher, M. H., Theoretical and Applied Colloid Chemistry, p. 20, (John Wiley & Sons, Inc., New York).

exists in the spheroidized steel were used as a standard, the Eggertz colorimetric test would show only missing carbon and no excess carbon, since the iron carbide particles would always be smaller.

In conclusion, the findings of this portion of the investigation indicate that the variation in the color carbon content of the Eggertz colorimetric carbon test is due entirely to the comparison of the iron carbide particle size and not to any other factors. These findings also show that the coloration of the acid solution increases progressively with the size of the carbide particle or, vice versa, decreases with the size of the iron carbide particles.

Heat Treatment and Aging

Since the color carbon test is dependent upon the particle size of the iron carbide particles, if all other things are equal, it seemed logical to assume that if aging in plain carbon steels were due to carbide precipitation and agglomeration, this test would indicate it. Therefore, duplicate series of quenched and tempered specimens of Steel A were examined for color carbon after 10, 30, 180, 360 and 550 days' aging at room temperature. The results obtained after a year and a half aging at room temperature are shown in Table I and Fig. 4.

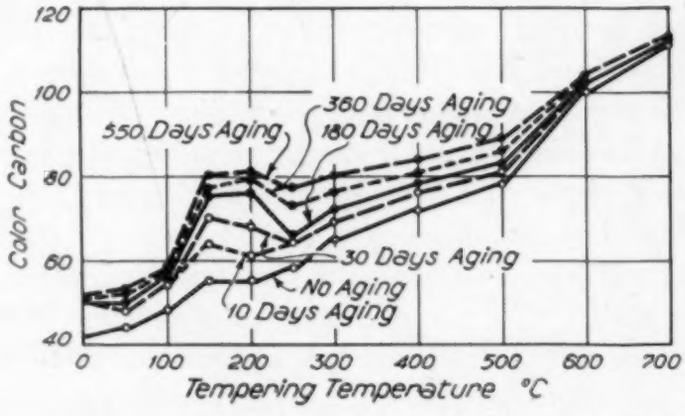


Fig. 4—The Effect of Aging Upon the Color Carbon of Tempered Steels.

Fig. 4 indicates that in quenched and tempered steels, carbon (carbide) is the direct cause of aging since aging results in an increase in the size of the iron carbide particles.

Aging in quenched and tempered carbon steels seems to imply supersaturation, precipitation and coagulation of the solute particles

(iron carbide) in the ferrite matrix. This process of agglomeration (aging) may be influenced by (a) the gases in solution, such as oxygen, nitrogen, etc., (b) the metallic alloying elements in solution; e.g., chromium, nickel, manganese, etc., and (c) the nonmetallic alloying elements in solution, such as phosphorus, sulphur, etc. These factors may either intensify or minimize the rate of precipitation and

Table I

Effect of Aging on the Color Carbon of Hardened and Tempered Steel (0.87 Per Cent Carbon)

Tempering Temperature Degrees Cent.	Aging Period at Room Temperature, Days					
	0	10	30	180	360	550
Room Temp.	0.42	0.48	0.50	0.50	0.51	0.52
50	0.44	0.48	0.48	0.50	0.52	0.53
100	0.48	0.54	0.54	0.56	0.58	0.58
150	0.55	0.64	0.70	0.75	0.77	0.80
200	0.55	0.61	0.68	0.76	0.79	0.81
250	0.58	0.64	0.64	0.66	0.73	0.77
300	0.65	0.69	0.69	0.72	0.76	0.80
400	0.72	0.76	0.76	0.78	0.81	0.84
500	0.78	0.81	0.81	0.83	0.86	0.88
600	1.00	1.02	1.02	1.02	1.04	1.04
700	1.11	1.12	1.12	1.12	1.13	1.13

agglomeration and naturally tend to determine the aging rate and characteristics of the steel. However, in quenched and tempered carbon steels, carbon which exists in the form of iron carbide $(Fe_3C)x$ seems to be the direct cause of aging and the manner in which the above mentioned factors affect it has not been determined. These results are in agreement with the findings of Pfeil[7] who showed that (a) carbon-free iron is not subject to aging, (b) iron containing as little as 0.0025 per cent carbon exhibits aging and (c) age-hardening is influenced by the presence of carbon.

Table I and Fig. 4 also indicate that aging is a function of time, temperature and particle size and is never complete. If the time and temperature are constant, the rate of agglomeration is determined by the size of the solute particle since fine-grained aggregates possess a greater initial rate of agglomeration than relatively coarse ones. This tendency decreases as coagulation continues.

Briefly, in hardened and tempered steel, aging is most marked in the steels tempered between 150 and 250 degrees Cent. (300 and 480 degrees Fahr.) and may be ascribed to the decomposition of retained austenite into martensite with precipitation and agglomeration. The

[7]Pfeil, L. B., *Journal*, Iron and Steel Institute, 1928, No. II, p. 167.

aging ability of the quenched steel above this tempering range decreases progressively with the higher tempering temperatures.

Rockwell hardnesses taken upon the above specimens after each aging period (0, 10, 30, 180, 360 and 550 days) are shown in Fig. 5 and Table II.

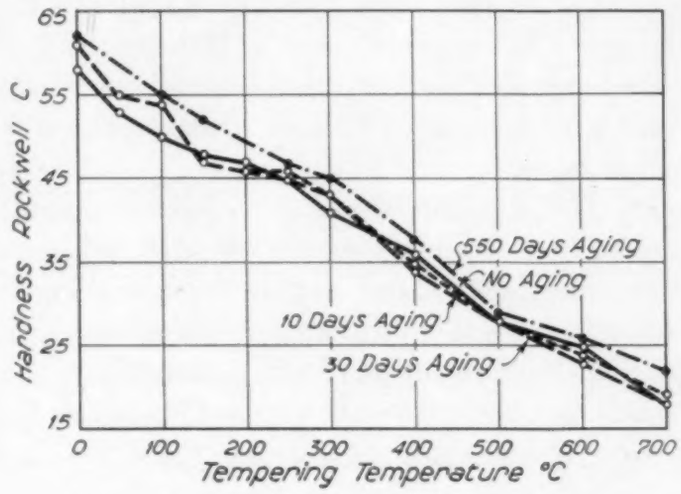


Fig. 5—The Effect of Aging and the Hardness of Tempered Steels.

Although the aging characteristics of a material may be observed by hardness readings, it is an indirect method of determining the rate of precipitation and agglomeration since the hardness readings meas-

Table II
Effect of Aging on the Hardness (Rockwell C) of Hardened and Tempered Steels (0.87 Per Cent Carbon)

Tempering Temperature Degrees Cent.	Aging Period at Room Temperature, Days					
	0	10	30	180	360	550
Room Temp.	58	61	61	61	62	62
50	53	55	55	54	55	55
100	50	54	54	53	55	55
150	48	47	47	48	52	52
200	47	46	46	46	47	47
250	45	46	45	44	45	47
300	41	43	43	42	44	45
400	36	35	34	32	38	38
500	28	28	28	25	28	29
600	25	24	23	23	25	26
700	18	19	18	17	20	22

ure only the effect of aging and not the actual phenomenon as revealed by the color carbon test. Moreover, the degree of aging cannot be computed from the hardness increase since hardness is only a relative measurement and is affected by the hardness of the original unaged specimens, inasmuch as an increase from 4 to 6 points on the

low side of the Rockwell "C" scale may not be equivalent to one point on the high side of the scale (Rockwell "C" 65 to 66).

To determine the effect of quenching and tempering temperatures upon the aging characteristics, series of specimens were quenched from below the thermal critical range 600 to 1000 degrees Cent. (1110 to 1830 degrees Fahr.) and tempered by small temperature intervals up to 700 degrees Cent. (1290 degrees Fahr.). The specimens were examined for hardness immediately or within two hours after heat treatment, aged 10 and 30 days respectively and re-examined for hardness.

A summary of the results shows that maximum aging occurs in steels when quenched from below the thermal critical range and minimum from immediately above and, as the quenching temperature is raised above the thermal critical range, the aging capacity of the steel increases with the amount of retained austenite.[1]

The Effect of Cold Work and Aging Upon Color Carbon

Since Sauveur[4] and Whiteley[5] showed that the type of cold work affects the color carbon readings in different manners, one series of steels were cold-worked by reduction (hammer) and another series by torsion.

To note the effect of cold work (reduction), specimens (1x1x½ inch) were heat treated to ranges from a martensitic to a spheroidized condition and were cold-worked upon an anvil to one-quarter and one-eighth inch thickness respectively. Cold work upon the martensitic steel was performed by the application of a 100,000-pound load (compression) for 30 minutes and removed. All specimens were analyzed for carbon immediately after cold work, aged 30 days at room temperature and re-examined for color carbon.

The color carbon results obtained upon the cold-worked and aged specimens tabulated in Table III show that the particle size of the iron carbide particles become smaller with increasing amounts of reduction with the exception of the martensitic steel which shows an increase of color carbon after compression. Table III also shows that, for constant reduction, the prior structural condition determines the relative size of carbide particles since the larger particles are reduced to a greater extent than the smaller. This is indicated by the color carbon loss in the 50 per cent reduced sorbitic, pearlitic and spheroidized steels which are 10, 15 and 22 points, respectively.

Table III
The Effect of Cold Work Upon the Color Carbon of Heat Treated Steel

Heat Treatment	Per Cent Reduction	Color Carbon 0 Days	Color Carbon 30 Days Aging
Martensitic	0	0.42	0.50
Martensitic	*	0.63	0.67
Sorbitic (Air-cooled)	0	0.76	0.79
Sorbitic (Air-cooled)	25	0.70	0.81
Sorbitic (Air-cooled)	50	0.66	0.79
Pearlitic	0	0.87	0.87
Pearlitic	25	0.81	0.85
Pearlitic	50	0.72	0.82
Spheroidized	0	1.24	1.24
Spheroidized	25	1.11	1.14
Spheroidized	50	1.02	1.09

*100,000 pounds load applied for 30 minutes.

Upon aging these cold-worked specimens at room temperature for 30 days and analyzing for color carbon, the results show (Table III) that (a) the more severely worked specimens exhibit maximum aging, (b) the original prior structural condition influences the rate of agglomeration, (c) martensitic steels which were subjected to compression age very little after 30 days' aging since maximum agglomeration seems to have occurred during compression.

The effect of torsion upon the particle size of the carbide particle was next studied. The torsion machine was of a constant loading type and the rate of loading was very slow (1 pound per minute). Series of torsional specimens were given different heat treatments and were tested both at room and elevated temperatures. When heated at elevated temperatures, the specimens were air-cooled to room temperature. The fractured surfaces of all tests were milled and analyzed for color carbon. Some of the results obtained on heat treated specimens fractured at room temperature, after torsion, are shown in Table IV.

Table IV
The Effect of Cold Work (Torsion) on the Color Carbon Content of Heat Treated Steels

Heat Treated Condition	Color Carbon (Per Cent) Tempered (Unworked)	Tempered and Cold-Worked
Martensitic	0.42	0.50
Sorbitic (Air Cooled)	0.76	0.82
Pearlitic	0.87	0.90

Table IV shows that cold work by torsion increases the coloration, or carbide particle size; whereas, cold work by reduction (ham-

mer) reduces the size of the iron carbide particles (Table III). Drilling acts in the same manner as torsion. These results definitely establish Whiteley's previous observations that different types of mechanical deformation affect the color carbon readings in opposite manners as shown above.

To summarize the effect of cold work and aging upon the size of the iron carbide particles, as determined by the color carbon test, it may be stated that the degree of aging in cold-worked steels depends upon the prior structural condition and the amount and type of deformation. Cold work by reduction (hammer) reduces the size of the carbide particles, distorts the ferrite lattice and increases the susceptibility to aging.

Cold work performed by torsion may act in a similar manner to that performed by reduction (hammer) but as the carbide particles are reduced to a lesser degree than in reduction, aging results immediately in an increase of particle size and consequently color carbon; whereas, in reduction, the decrease in the carbide particle size is so drastic that even though immediate and subsequent aging does increase the particle size (color carbon), it never reaches its original size. Therefore, the Eggertz colorimetric carbon test always shows missing carbon. This hypothesis explains the apparent loss (missing carbon) and gain (excess carbon) in color carbon in these two types of cold work.

Part II

The Aging of the Iron Carbide Aggregates

Since the effects of heat treatment, aging and working upon the size of the iron carbide particles were determined by chemical and physical tests in the preceding pages without any direct reference to the iron carbide aggregates, this portion of the paper deals with the aging of the various aggregates formed in steel by thermal treatment.

Steel essentially is an alloy of iron and carbon (carbide) and must exist either as a solid solution or as an aggregate of two or more phases. Therefore, the various structural phases which are formed in steel may be classified as follows under two categories:

I. *Solid Solutions*

(a) Solid solution of carbon in alpha or delta iron (ferrite).

(b) Solid solution of carbon in gamma iron (austenite).

(c) Solid solution of carbon in tetragonal iron (martensite).

II. *Aggregates*

(a) Solid solution aggregates.

(b) Lamellar aggregates.

(c) Granular or spheroidal aggregates.

Inasmuch as the solid solutions recorded under category I are too well known to merit much discussion, the various aggregates of steel tabulated above are described briefly in the following paragraphs.

Solid solution aggregates are aggregates of two or more solid solutions whose physical, chemical, electrical and structural properties are different. This type of aggregate is readily formed at elevated temperatures in most types of steel or at room temperature in alloy steel by having two or more of the above mentioned solid solutions together.

Lamellar aggregates are obtained by cooling from above the thermal critical range any alloy of iron and carbon which contains more than some 0.035 per cent carbon (the limit of solid solubility of carbon in alpha iron at the A_1 point) at a cooling rate less than the critical rate of cooling which yields martensite. The microstructure of the carbide particles obtained in the residue of steel dissolved in cold diluted nitric acid (1.2 specific gravity) is shown in Fig. 6. This photomicrograph reveals the lamellated structure of the carbide particles themselves which is normally observed in the microexamination of polished and etched steels.

Granular or spheroidal aggregates are obtained by tempering any alloy of iron and carbon at subcritical temperatures in order to coalesce the iron carbide particles and form an aggregate of cementite (granular or spheroidal) in ferrite. The microstructure of the carbide particles obtained in the residue of hardened and tempered steels is shown in Fig. 7. These two photomicrographs (Figs. 6 and 7)

Table V

The Nomenclature of the Iron Carbide Aggregates

Lamellar	Carbide Particle ↓ Size Decreases	*Granular*
Pearlite		Spheroidized Cementite
Sorbite		Sorbite
Troostite		Troostite
Martensite		Martensite

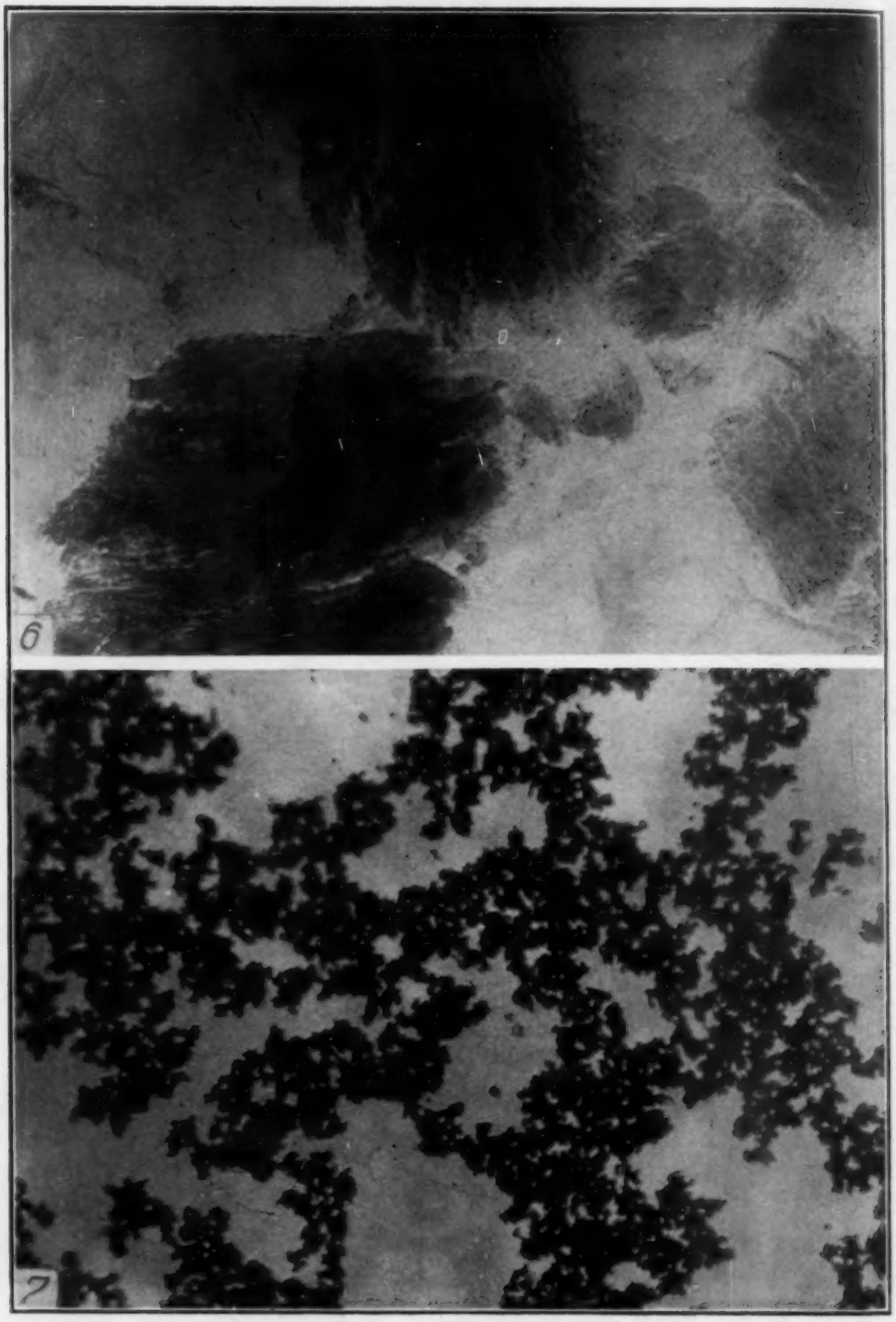


Fig. 6—Micro-structure of the Iron Carbide Residue Obtained After Dissolving Normalized Eutectoid Steel in Cold Diluted Nitric Acid. × 1750.

Fig. 7—Micro-structure of the Iron Carbide Residue Obtained After Dissolving Hardened and Tempered (Sorbitic) Eutectoid Steel in Cold Diluted Nitric Acid. × 1750.

reveal the physical and structural differences in the carbide structure of the lamellar and spheroidal aggregates.

Since the various structural conditions of iron and carbon (carbide) obtained by thermal treatment in steel have been described above, the accepted nomenclature generally used to identify these states of carbide dispersion in ferrite is shown in Table V.

In Table V the carbide particles decrease from pearlite to martensite and from spheroidized cementite to martensite, respectively. Hence, the nomenclature in the above table represents various degrees of dispersion of carbon (carbide) in ferrite with no definite line of demarcation between each succeeding aggregate, since the increase or decrease in the size of the carbide particles is progressive.

The Causes of Aging

Before discussing the various causes of aging in the iron carbide aggregates, it seems advantageous and appropriate at this time to define aging since it is generally used in a number of manners.

Aging: In a broad sense, aging implies any change that occurs in either the physical, chemical, electrical or structural condition of the material under consideration with the passage of time at normal atmospheric temperature (room temperature) or elevated temperatures. However, for accuracy, aging at normal atmospheric temperature (room temperature) should be termed "normal aging," while aging at temperatures above or below room temperature should be designated as "artificial aging."

Precipitation Aging: When any change occurs in either the physical, chemical, electrical or structural condition of the material under consideration with the passage of time, and results directly from the precipitation of a substance or substances (solute or solutes) from the matrix of the material (solvent), it should be called "precipitation aging." Therefore, it seems logical to conclude that if this type of aging occurs at room temperature it should be designated as "normal precipitation aging" or "artificial precipitation aging" if it takes place either above or below room temperature.

Strain Aging: When mechanical deformation imparts the susceptibility to age at room temperature, it is usually termed "strain aging." However, when heated above room temperature and grain growth or grain refinement occurs, it should be called "recrystallization" since it is no longer an aging phenomenon.

Since aging was defined in the above paragraphs, the reason of aging in the iron carbide aggregates is now discussed. But before presenting the aging characteristics of the various iron carbide aggregates, it should be stated that aging in steel is primarily a precipitation phenomenon and may result from any of the following reasons:

(1) Limited solubility: The solid solubility of carbon in alpha iron decreases progressively from approximately 0.035 per cent at the lower limit of the thermal critical range (A_1) to some 0.006 per cent at room temperature.

(2) Allotropism: The transformation of one lattice to another usually occurs with a change in solid solubility. This is particularly true in alloys which transform from body-centered to face-centered cubic lattices since the face-centered structure possesses the greatest dissolving power of any of the material's polymorphic forms. This especially pertains to steel since austenite (face-centered cubic) can retain approximately 1.7 per cent carbon in solution while ferrite (body-centered cubic) can only dissolve a maximum amount of approximately 0.035 per cent at the A_1 point or about 0.006 per cent carbon at room temperature.

(3) Mechanical deformation: Cold work will usually cause aging by shifting the solid solubility slightly to the left thereby causing precipitation and subsequent aging.

(4) Diffusion: Precipitation aging may occur by heating an alloy in contact with a substance such as a gas, metal, compound or solid solution which diffuses into the alloy and affects the solid solubility. Consequently, when the metal is cooled to room temperature, supersaturation and precipitation result in aging. This occurs primarily in carburizing, nitriding, or in any process of impregnation where the solubility at elevated temperatures is greater than at room temperature.

To complete the picture of precipitation aging, it should be mentioned also that in some alloys, other than steel, aging occurs by heating metastable solid solutions or variable compounds at definite temperature ranges in order to form superstructures or other compounds. This also is a form of precipitation aging since the structural change is almost always accompanied by precipitation.

When steel is heat treated in any condition, the affinity of the resultant aggregate to age is controlled by the factors enumerated above. Consequently, aging in steel is controlled by (1) the amount of retained austenite, (2) the amount of carbon dissolved in alpha

iron, (3) the size of the iron carbide particles, (4) time and temperature of tempering and (5) the degree of mechanical deformation remaining within or conferred upon the specimen after the final heat treatment.

The Aging of the Aggregates

To determine the aging characteristics of the various aggregates, series of annealed specimens of Steel A (0.87 per cent carbon) were heat treated so as to form the different aggregates in steel and aged at room temperature 10 and 30 days respectively. The color carbon readings (average of 6 determinations) were taken immediately after heat treatment and after each aging period. The results are tabulated in Tables VI and VII.

Table VI
The Effect of Aging on the Color Carbon Readings of the Lamellar Aggregates

Structure	Days Aging at Room Temperature 0	10	30
Martensite (H_2O Quenched)	0.42	0.46	0.49
Troostite (Oil-Quenched)	0.52	0.64	0.71
Sorbite (Air-Cooled)	0.76	0.79	0.84
Pearlite (Furnace-Cooled)	0.87	0.87	0.87

Table VII
The Effect of Aging on the Color Carbon Readings of the Spheroidal Aggregates

Structure	Days Aging at Room Temperature 0	10	30
Martensite	0.42	0.46	0.49
Martensite + Troostite	0.55	0.63	0.69
Troostite	0.72	0.75	0.80
Sorbite	1.00	1.02	1.02
Spheroidized Cementite	1.24	1.24	1.24

From the results of Table VI and VII and the previous findings given in Part I of this paper, the aging characteristics of the various aggregates formed in carbon steels of eutectoid composition are now considered. These characteristics may also apply to hypo- and hypereutectoid steels, but must be slightly modified since hypoeutectoid steels age more than eutectoid which in turn ages more than the hypereutectoid compositions, inasmuch as the amount of ferrite tends to regulate the degree of aging.

Austenite: Since a completely austenitic condition can never

be retained at room temperature in plain carbon steels, the normal aging characteristics of austenite are deduced from its behavior in martensitic or troostitic steels which are obtained either by water or oil quenching. Its characteristics may also be observed from the decomposition of austenitic alloy steels upon heat treatment.

Retained austenite in quenched carbon steels is unstable and subsequent tempering causes it to transform into an aggregate of ferrite and cementite whose state of carbide dispersion is a function of tempering time and temperature. But, regardless of time and temperature, the initial step in the austenitic decomposition is an atomic rearrangement, or lattice change, from face-centered cubic to body-centered cubic. This transformation is accompanied by supersaturation since the carbon retained in the austenite is retained momentarily in solution in the ferrite before precipitation occurs. At the first instance of precipitation, the carbide particles are precipitated in a submicroscopic state of division, and agglomeration occurs as rapidly as time and temperature permit. Hence, austenite transforms immediately upon tempering into martensite which in turn may be converted into a coarser state of division, such as troostite, sorbite or spheroidized cementite or, more simply, into an aggregate of granular (spheroidal) cementite in ferrite whose carbide particle size is determined by the time at temperature and temperature of aging (tempering).

Another factor worthy of mention which influences the decomposition of retained austenite upon tempering is the temperature from which the steel was hardened since the higher quenching temperatures seem to yield a more stable austenite than the lower temperatures and subsequent artificial aging (tempering) results in a greater hardness increase for constant aging time. Finally, the austenitic grain size influences the ultimate aging characteristics and it seems that a coarse grain structure acts like steels hardened from a higher temperature. They tend to resist transformation more so than fine-grained austenite and, consequently, yield a greater hardness increase than fine-grained material upon decomposition.

Martensite: Inasmuch as a 100 per cent martensitic structure is never obtained by quenching a carbon steel, but an aggregate of martensite and retained austenite, the aging characteristics are affected by two factors; namely, (1) the percentage of retained austenite and (2) the aging characteristics of martensite. Neglecting the presence of retained austenite for the time being, martensite may be

considered as a fully aged constituent, as proposed by Professor Sauveur,[8] and subsequent aging either at room or elevated temperatures will result in coagulation of the submicroscopic carbide particles precipitated during hardening in the quenching bath. If aging occurs at or slightly above room temperature, the hardness may gradually increase until a critical dispersed submicroscopic carbide particle size is reached. Continued aging will then cause a progressive decrease in hardness.

When the martensitic aggregate composed of retained austenite and martensite is aged normally at room temperature or artificially at elevated temperatures, not above the martensite-troostite temperature change, the decrease in hardness due to agglomeration in the martensitic structure is over-shadowed by the increase created by the austenite-martensite conversion. The resulting hardness increase by this conversion is determined, as before mentioned, by the aging time and temperature.

In discussing the consequence of aging upon martensite in the preceding paragraphs, the structural variations of this aggregate were omitted from consideration. However, since the structural composition of the aggregate seems to influence the aging characteristics of martensite, the effects of these variations were carefully studied by dissolving in cold diluted nitric acid (1.2 specific gravity) series of heat treated eutectoid specimens and examining the carbide precipitate, obtained by this method, microscopically on thin biological slides. By this procedure, the carbide structure of the hardened steel could be readily ascertained, whereas, in the hardened steel specimen, it is impossible to determine microscopically the form and structure of the carbide particles.

The results obtained by this method of carbide examination definitely show that two distinct forms of martensite exist: (1) the lamellar or acicular type that is formed in quenched martensite and (2) the granular or spheroidal type which occurs in slightly tempered martensite. The former—the lamellar or acicular type—exists only in the "as-quenched" condition and tempering for even as short a duration as 2 hours at 100 degrees Cent. will convert the acicular carbide structure into the spheroidal form. Continued tempering increases the size of these spheroidal precipitates.

These results seem to indicate that the carbide structure in quenched martensite is lamellar in form and submicroscopic in size

[8]Sauveur, A., *Metals and Alloys*, August 1932.

since the state of division of the cementitic plates become progressively finer and finer with the rate of cooling until they remain entirely in solution in martensite (solid solution of carbon in tetragonal iron) or austenite (solid solution of carbon in gamma iron).

Since the structure of the acicular carbide particles was so markedly affected by such a short tempering treatment, it seemed worthy to study the effects of aging upon the carbide structure of quenched steels. Therefore, series of small eutectoid specimens were hardened and aged at room temperature for 0, 10, 30 and 60 days. After aging, the entire series was dissolved in cold diluted nitric acid and the carbide precipitates were examined microscopically. A comparison of the 0, 10 and 30-day aged specimens showed that the 30-day aged steel was slightly different in carbide structure from the "as-quenched" and 10-day aged specimens which were similar to each other. The structure of the 30-day-old precipitates was reefy and not so acicular as in the specimens aged 0 and 10 days respectively. This change was more intense in the specimen aged 60 days at room temperature and indicated that surface tension tends to coalesce the carbide particles from the acicular to the spheroidal form of structure in aged martensite.

To complete the effect of aging upon the structure of hardened steels, the series of quenched steels which were examined in 1931 for color carbon and the effect of aging upon color carbon in Part I of this paper were re-examined in 1937 for carbide structure after being aged slightly more than six years at room temperature. The microscopic examination of the carbide particles of the steels aged six years at room temperature, after dissolving in cold diluted nitric acid, showed them to be completely spheroidal in form without any trace of aciculation. These steels further indicate that aging at room temperature is an agglomeration process since it coalesces the acicular carbide particles of martensite into spheroidal cementite by means of surface tension.

A comparison of the above results with those observed and recorded in the first portion of this study show that aging is an extremely mild form of tempering and that the mechanism by which the acicular carbide structure of quenched steels changes during aging to the spheroidal form is similar to that observed in the spheroidization process of pearlitic steels during tempering.

Troostite: The aging characteristics of troostite obtained by oil quenching and those of troostite formed by the decomposition of

martensite and retained austenite by tempering are entirely different. The troostitic aggregate created by quenching possesses more retained austenite, a greater saturation of carbon in ferrite and a smaller carbide particle size than the troostitic aggregate formed by tempering. As a result of these factors, the former has a greater urge to age than troostite obtained by tempering as is shown in Tables VI and VII where the color carbon increase for 10 and 30 days aging respectively are 12 and 19 points carbon against 3 and 8 points in the troostitic condition or 8 and 14 points for the martensitic-troostitic condition.

Sorbite: Normalizing an aggregate whose solid solubility decreases toward room temperature creates a tendency for supersaturation and a smaller particle size than is ordinarily retained by slow cooling, which tends to create equilibrium conditions. Consequently, such an aggregate will respond to aging. This particularly is true of sorbite obtained by air cooling as is shown in Table VI.

Sorbite formed by the decomposition (tempering) of austenite and martensite is not so susceptible to aging as normalized sorbite, since most of the aging constituents are removed. However, a very slight amount of aging does occur but not to any extent as is shown in Table VII.

Spheroidized cementite: This aggregate of spheroidal cementite in free ferrite should be the most stable of all the different structural compositions obtained by thermal treatment in iron and steel if complete spheroidization of all the carbide particles occur. But, nevertheless, aging may proceed very slowly since there does not seem to exist any ultimate size for the carbide particles.

Pearlite: Although this aggregate is the last to be discussed, it is one of the utmost importance and, in recent years, has been the subject of much discussion in certain portions of the metallurgical world. Pearlite is an aggregate of cementite lamellae in a ferritic matrix and is chemically and structurally of eutectoid composition, inasmuch as the proportion of free ferrite to cementite is in the approximate ratio of 6.5 to 1. However, when the rate of cooling from above the critical is increased from slow furnace cooling to drastic quenching, these coarse cementite lamellae progressively become finer and finer until they remain entirely in solution. Consequently, this increased state of dispersion of the cementite lamellae destroys the normal structural proportions of approximately 6.5 parts of ferrite to 1 part of cementite and concurrently changes the com-

position of ferrite from free ferrite (which is normally supposed to contain some 0.006 per cent carbon in solution at room temperature in furnace cooled pearlite) to a supersaturated solid solution of carbon in alpha iron whose state of saturation is determined by the rate of cooling. Thus, the question of discussion, mentioned above, is whether the term "pearlite" should apply to all the various states of dispersion of the cementite lamellae, irrespective of structural proportions of free ferrite to cementite and carbon concentration in the ferrite, or only to the aggregate formed by slow cooling which meets the above requirements and to which the original name of "pearlite" was given.

Regardless of the above nomenclature discussion, aging in pearlitic steels is a function of (1) the state of division of the cementite lamellae and (2) the carbon concentration of the ferrite. These two factors work in conjunction with one another and, as the carbon concentration of the ferrite or the state of division of the cementite lamellae increase, the aging propensities of the aggregate automatically become greater. This fact is shown in Table VI where the color carbon readings of the pearlitic, sorbitic and troostitic steels after aging 30 days at room temperature are 0, 8 and 19 points respectively.

Theory of Aging: The findings of this investigation dealing with the effects of thermal and mechanical treatment upon the aging propensities of steel substantiate the precipitation theory of Professor Sauveur.[8] They indicate that aging is a precipitation phenomenon and results from the precipitation and agglomeration of the iron carbide particles. This phenomenon may be accelerated or retarded by the presence of other alloying elements which may either assist or retard the rate of precipitation and agglomeration and, thereby, act as either negative or positive catalysts.

The aging characteristics of the various aggregates obtained by thermal treatment in steel are in general a function of carbide particle size and the amount of carbon retained in the alpha iron solid solution (ferrite). These two conditions work concurrently and, when the iron carbide particle size decreases, the amount of carbon retained in ferrite increases. Consequently, the aging ability of the various aggregates increases with the rate of cooling from above the thermal critical range or decreases with the degree of tempering below the thermal critical range. Thus, in the lamellar family, martensite ages during quenching, troostite (oil-quenched) ages more than sorbite

(air-cooled), which in turn ages more than pearlite (furnace-cooled); whereas, in the spheroidal aggregates, the martensitic-troostitic aggregate ages more than the troostitic which responds more quickly to aging than either sorbite or spheroidized cementite. However, aging is never complete since no ultimate size of the iron carbide particles seems to exist.

General Discussion

Although many facts were brought out in this report, the most pertinent findings were casually mentioned in the first part of the paper. These findings are extremely important from the metallurgical and, especially, from the chemical point of view.

From the chemical standpoint: The volumetric method of analyses is markedly affected by the size of the dissolving particles and, for certain acid concentrations (constant dissolving time, temperature and volume of acid), erroneous results will be always obtained if any variation in particle size exists. These facts have been shown by the color carbon test throughout this report and will be subsequently illustrated by other determinations.

From the metallurgical standpoint: The volumetric method of determination presents a method by which the relative size of the dissolving particles may be measured and the effects of thermal, mechanical and aging treatment ascertained. These facts have been shown consistently throughout this report dealing with the effects of heat treatment, working and aging upon the condition of carbon in steel.

To note whether the above contentions held true in other volumetric determinations, series of tests were run over a period of years whenever the opportunity for them was present. The first of these tests was made for the writer by Dr. Joseph Clough (Doctorate's Thesis, Harvard University, 1933) on nitrogen. Nitrided specimens of Armco iron were quenched from above its critical and analyzed for nitrogen by the volumetric-titration method. The quenched specimen showed 0.37 per cent nitrogen (average of 3 tests). The same specimen was then tempered and re-analyzed for nitrogen. The test showed only 0.17 per cent nitrogen instead of 0.37 per cent, or a loss of 0.20 per cent. These results were surprising since they acted entirely opposite to color carbon test where quenching yields "missing carbon" and tempering "excess carbon"; whereas, in the nitrogen

test, quenching yields "excess nitrogen" and tempering "missing nitrogen."

The investigation of excess and missing nitrogen was continued a few years later on all types of chromium alloys which contained appreciable amounts of nitrogen. The results obtained were consistent throughout and are illustrated in Table VIII. The four steels investigated in this table were all of the NCR 819 type (8:19(Ni:Cr) modification).

Table VIII shows that the coarse size particles (air-cooled) yield the least amount of nitrogen and, as soon as the size of the particles becomes smaller (oil-quenched), the percentage of nitrogen increases. Cold working further accentuates this difference since it also tends to refine the particle size and increase the rate of dissolution. To note whether the prior heat treatment affected the nitrogen

Table VIII

The Effect of Thermal and Mechanical Treatment Upon Nitrogen in Steel as Determined by the Volumetric-Titration Type of Test

Treatment	Steels			
	A	B	C	D
	Per Cent Nitrogen			
Air-cooled	0.050	0.050	0.049	0.050
Oil-quenched	0.055	0.056	0.052	0.051
Oil-quenched and cold-worked	0.064	0.061	0.056	0.055
Oil-quenched and cold-worked and normalized	0.050	0.050	0.049	0.050

content, the oil-quenched, cold-worked specimens were normalized and re-examined for nitrogen. The results checked those of the normalized specimens and showed that the prior structural condition does not affect the nitrogen content of the material. All these results, however, reveal that the nitrogen determination is influenced by the size of the nitride particles and that the finer particles yield a smaller calculated percentage of nitrogen than the coarser.

At first no explanation could be offered to account for this phenomenon but, after a careful study of the nitrogen test, the reason became quite apparent. In the colorimetric (color carbon) test, the smaller particles yield less coloration than the coarser: consequently, hardened steels reveal "missing carbon" and tempered steels "excess carbon." In the volumetric-titration test (nitrogen), the smaller particles go into solution faster and yield more ammonia (NH_3) gas in a shorter period of time than the coarser aggregates. Consequently, upon titration, the increased volume of gas requires a greater volume of acid to neutralize it. As a result, when the titrational

volume is converted into per cent element present, the finer particle sizes yield more calculated nitrogen than the coarser particles.

To ascertain whether the above variations in nitrogen content were due to incomplete solution of the nitride particles or to their dissociation, series of normalized specimens were permitted to remain in the acid solution (1:1 HCl), prior to heating, from one-half to 24 hours. The results obtained, after analysis, showed that the amount of calculated nitrogen increased progressively with time until approximately the same amount was recorded as in the quenched and cold-worked specimens. These findings indicate that incomplete solution occurred when the coarse particles were analyzed by the regular method of analysis and that a longer dissolving time is required to complete solution. Therefore, it would seem most logical to conclude that these variations could be eliminated entirely by permitting the specimens to remain in the acid solution overnight in order to complete solution. Unfortunately, the matter is not so simple since some coarse-grained steels never go completely into solution in the hydrochloric acid and, consequently, always show a lower calculated percentage of nitrogen present. Another factor of importance, which must be taken into consideration, is that the procedure employed must be standardized for routine analysis and a constant dissolving time used. Thus, if too long a time is permitted, the fine-grained steels lose nitrogen: whereas, the coarse-grained steel gains nitrogen. If the duration is too short, the opposite is true. Therefore, to eliminate these discrepancies, it is very essential to heat treat all specimens alike (constant time and temperature) and to employ the same duration of dissolving time throughout in order to obtain relative results.

In concluding the above brief discussion of the effects of particle size upon the volumetric tests, it may be stated that the colorimetric and titration tests act opposite to each other in regard to the effect of particle size upon the final results since a smaller particle size yields a lower calculated percentage of the element present in the colorimetric test and a larger percentage in the titration test. In order to eliminate these variations in the different tests, all specimens should be similarly heat treated. In the colorimetric test, the specimens should always be in the annealed condition; whereas, in the titration test, the steels should be normalized from a high temperature. However, in both volumetric tests, the results are only relative and do not indicate the true percentages of the element present in the material as in the gravimetric methods of determinations.

Before closing, the writer wishes to state that variations have also been observed in the colorimetric test for molybdenum but sufficient data have not been accumulated to show the intensity of these variations in the different molybdenum steels at the present time.

Summary

Part I

1. The color carbon test for combined carbon in steel shows that three structural changes occur in the size, form and structural composition of the carbide particles and in the nitric acid solution when hardened and tempered steels are dissolved in cold diluted nitric acid (1.2 specific gravity). The temperature ranges of these changes extend (a) from the as-hardened condition to 250 degrees Cent., (b) from 250 to 400 degrees Cent., and (c) above 400 degrees Cent. These structural changes represent the martensitic, troostitic and sorbitic conditions of steel and reveal that each of these aggregates possesses certain definite chemical and structural characteristics which are easily distinguishable by the color carbon test.

2. The coloration of the dilute nitric acid solution (1.2 specific gravity) formed during the Eggertz colorimetric carbon test for combined carbon, before or after boiling, is due to a colloidal solution of either iron or iron carbide in nitric acid. This colloidal solution may be divided by means of dialysis into three parts which indicate the various states of dispersion from the coarse dispersions—colloids—to the molecular dispersoids.

3. The coloration of the nitric acid solution used for the determination of combined carbon in steel is a function of the size of the iron carbide particles since the finer carbides dissolve more rapidly than the coarser and, consequently, the coloration of the acid solution varies directly from yellowish-green in martensite to deep brown in spheroidized cementite.

4. "Missing carbon" is the amount of carbon that is not recorded when a steel is compared volumetrically against its standard and results from the colorimetric comparison of a smaller particle size against a larger. The amount of missing carbon depends upon the ratio of carbide particle size between the standard and unknown.

5. "Excess carbon" is the amount of carbon that is recorded in excess of that contained on the standard (annealed) of the same steel. "Excess carbon" results from the volumetric comparison of a larger

carbide against a smaller (standard) and the amount of excess carbon depends upon the ratio of particle size between the unknown and the standard.

6. Aging over a period of 550 days indicates that carbon seems to be the direct cause of aging in carbon steels since the size of the carbide particles increases with aging.

7. Aging in carbon steels seems to be a precipitation phenomenon and implies supersaturation, precipitation and agglomeration of the iron carbide particles.

8. Aging is never complete and is a function of time, temperature and particle size.

9. Maximum aging occurs in steels quenched from below the thermal critical range; while minimum aging occurs in steels hardened from immediately above the critical.

10. The aging ability of carbon steels increases with the amount of retained austenite.

11. Aging increases with the amount of mechanical deformation (cold work).

12. The aging propensity of cold-worked steels is markedly affected by the original size of the carbide particles since the finer carbide aggregates age much more rapidly than the larger carbide sizes.

13. Cold work affects the size of the carbide particles in two manners: It may either reduce the iron carbide particle size or increase it. Cold work by reduction reduces the size of the iron carbide particles; whereas, torsion, milling or drilling increase it.

Part II

1. The various structural phases of steel are classified into two categories: (a) solid solutions and (b) aggregates. The aggregates are in turn subdivided into the following divisions: (a) solid solutions, (b) lamellar aggregates and (c) granular or spheroidal aggregates.

2. After defining the various types of aggregates that are formed by thermal treatment in steel, the nomenclature applied to these different states of dispersion is briefly presented and discussed.

3. Aging in steel is a precipitation phenomenon and may result either from: (1) limited solubility, (2) allotropism, (3) mechanical deformation or (4) diffusion.

4. The aging characteristics of the various lamellar and spheroidal aggregates in steel are presented and discussed. The results obtained by means of the color carbon test show that aging in both the lamellar and spheroidal aggregates is a function of carbide particle size and the amount of carbon retained in ferrite.

5. Quenched nitrided or chromium steels containing appreciable amounts of nitrogen yield either "excess" or "missing" nitrogen, depending upon the comparison of particle size.

6. The volumetric method of analysis is a relative method of determining the percentage of element or elements present in steel since it is influenced by the size of the dissolving particles.

7. The volumetric-colorimetric method of test has a tendency to yield a lower calculated value the smaller the dissolving particles become; whereas, the volumetric-titration test yields a greater percentage of element present, the finer the dissolving particles become. This has been shown by the color carbon and nitrogen tests, respectively.

Acknowledgments

The author wishes to express his sincere gratitude for the counsel, pertinent suggestions and constructive criticisms throughout the course of this investigation that were rendered by Professor Albert Sauveur, then Gordon McKay Professor of Metallurgy and Metallography, Emeritus, of Harvard University (deceased). He also gladly acknowledges his indebtedness to the Council of the Iron and Steel Institute of England for the award of a grant from the Andrew Carnegie Research Fund, with the aid of which the first portion of this work was carried out. Mr. Reinhold Schempp, Metallurgist of the Halcomb Steel Division of the Crucible Steel Company of America, Syracuse, New York, is also thanked for his valuable discussions and comments during the latter part of this work.

DISCUSSION

Written Discussion: By E. G. Mahin, professor of metallurgy, University of Notre Dame, Notre Dame, Ind.

The attempt to obtain additional information concerning the fundamental causes of variation in the results obtained by the color method for carbon determinations is a commendable one. On account of the relatively short time required for a determination by this method it will continue to be widely used, especially for control work, yet the necessary precautions to be observed in

interpreting the results, especially in the selection of standard samples, occasionally tend to lessen confidence in the analytical results.

The investigation reported in this paper, also the results summarized in papers to which the author refers, seem to confirm the belief that most, if not all, of the color in the steel solution is due to carbon compounds (or elementary carbon?) in colloidal suspension. Since the color of sols is a function of the size of the molecular or atomic aggregates of the dispersed phase, it is not surprising to learn that the previous condition of carbon in the steel has a direct bearing upon both quality and intensity of color in the acid solution.

In the paper under discussion a fairly definite relation is shown to exist between color of solution and particle size of carbides. Large particles naturally dissolve more slowly than small ones, since the ratio of surface to mass is lower. Also the particle size of carbides is greater as the severity of quenching diminishes or as the tempering action increases.

The question might here be raised as to whether this relation between color and particle size may be incidental, rather than direct. Variation in rate of solution might directly affect the colloidally dispersed molecular aggregates but it should have no other effect, since the carbides are supposed to be in complete solution before the color comparison is made. On the other hand there is a direct—although not necessarily extremely definite—relation existing between average particle size and the previous thermal treatment of the steel. This has to do not only with definite crystals of the carbide phase but also with the atomic dispersion of carbon in alpha or gamma iron. Previous thermal treatment affects (1) the degree of supersaturation of carbon in alpha iron, (2) the proportion of retained austenite, if any, and (3) the degree of supersaturation of carbon in gamma iron.

It seems possible that the final color of the acid solution may depend partly upon this variation in carbon condition, as well as upon the amount and average crystal size of precipitated carbides. While such interdependence might not invalidate the general rule relating color to particle size, it would have something to do with the fundamental interpretation of the rule.

It should not be difficult to obtain light upon this phase of the question, possibly by the examination of austenitic carbon steel which has been drastically quenched in thin sections. Possibly the author already has some information concerning this point and the results of his observations should be of interest.

Written Discussion: By Dr. Albert Sauveur (Deceased).*

During the last decade of the last century "color" carbon and its complement, "missing" carbon, were receiving a great deal of attention among a small group of metallurgists, and interesting results were being reported. As so often happens, however, in similar instances, investigation in this field was abandoned, for no apparent reason, but so completely that younger generations of metallurgists hardly know the significance of the terms.

I, for one, welcome its revival, as I believe that further study in this field is still capable of yielding information of much value.

Dr. Shapiro's paper is a distinct advance in our understanding of the significance of color carbon. His results show conclusively that carbon steel,

*At the time this was written, Dr. Sauveur was associated with Harvard University as Gordon McKay Professor of mining and metallurgy.

whatever its composition and treatment, is always, barring the possible presence of some retained austenite, an aggregate of ferrite and of particles of the carbide Fe_3C and that steels differ from each other in properties chiefly, if not solely, because of the size of the carbide particles and of the ferrite grains, which vary according to carbon content, to thermal and to mechanical treatments, hardness and strength increasing as particle size and grain size decrease.

Dr. Shapiro's results clearly indicate that the intensity of the color in dissolving steel in dilute nitric acid is solely due to the *size* of the carbide particles. The color is minimum in martensite and increases steadily as, through agglomeration of the carbide particles, we pass through the troostitic and sorbitic stages, being maximum when the steel is spheroidized.

It is still occasionally stated by some that martensite is essentially a solid solution of carbon in alpha iron. That so excessively a supersaturated solid solution could exist seems highly improbable. It is much more logical, in view of our understanding of the aging phenomenon, to assume that this extremely supersaturated solid solution of carbon in alpha iron immediately begins to age in the quenching bath, through the precipitation of carbide particles submicroscopic in size, perhaps of so-called "critical size," causing very great hardness.

The belief that the carbon in martensite is present as submicroscopic particles of the carbide of iron rather than in solid solution seems to find a strong support in the results of the colorimetric determination of carbon which yields a decided coloration. If the carbon was in solid solution in alpha iron, it is believed that the color would be practically nil. Carbon in solution, whether in gamma or in alpha iron, imparts little if any color to the nitric acid solution.

It is suggested that the colorimetric method for the determination of carbon could be used to advantage, seeing that it yields information as to the size, relative at least, of the cementite particles, data not obtainable by microscopical examination, and bearing in mind the close relation between the particle size and the properties of the metal. It would in a way complement the determination of ferrite grain size by means of the microscope.

The study made by Dr. Shapiro of the aging phenomenon in the light of color carbon has yielded interesting and suggestive results. They should be closely studied by those who have investigated the aging of steel.

Author's Reply

In regard to Professor Sauveur's discussion, I have no comments to make since the discussion speaks for itself.

The experiments suggested by Professor Mahin were made a few years ago and are summarized briefly in the paper under discussion. These results, as stated in the paper, indicate that the controlling factor in the color carbon test is the size of the iron carbide particles since the carbon in solution in either ferrite or austenite does not impart any coloration whatever to the acid solution. This fact was brought out by Professor Sauveur in his discussion of martensite.

CONSTITUTION DIAGRAMS FOR IRON-CARBON-MOLYBDENUM ALLOYS

By J. R. Blanchard, R. M. Parke and A. J. Herzig

Abstract

Twelve constitution diagrams for the Fe-C-Mo system up to 1.2 per cent carbon and 6.0 per cent molybdenum were established from the microscopic and hardness examination of forty-one alloys. The diagrams show the structures found in the alloys as water-quenched from 1350, 1450, 1550, 1650, 1750, 1850 degrees Fahr. and as normalized from the same temperatures.

Introduction

In studying the effect of alloying elements in steel many metallurgists find the constitution diagram (in contradistinction to the equilibrium diagram) to be a useful and concise manner of describing the fundamental structures actually obtainable in a given alloy system after commercial heat treatments. The constitution diagrams for several of the common alloy systems, after at least one condition of heat treatment, are already available. This investigation is intended to establish such constitution diagrams for iron-carbon-molybdenum alloys, showing characteristic water-quenched and normalized structures obtainable after controlled heating to six representative temperatures in the range from 1350 to 1850 degrees Fahr. (735 to 1010 degrees Cent.). These constitution diagrams differ from those previously published on other ferrous systems in that the constituent, developed here by the presence of molybdenum, which forms at temperatures below that of pearlite formation and above that of martensite formation has been recognized and called bainite. For a description and identification of this micro-constituent the reader is referred to an article by J. R. Vilella, G. E. Guellich and E. C. Bain (13).[1]

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, J. R. Blanchard is metallurgical assistant, R. M. Parke is research metallurgist, and A. J. Herzig is chief metallurgist, Climax Molybdenum Company, Detroit. Manuscript received July 25, 1938.

Obviously the development and interpretation of constitution diagrams should be consistent with fundamental equilibrium conditions for the corresponding system. For this reason, the presentation of the constitution diagrams will include a review of the more important work on transformations and equilibria in the iron-carbon-molybdenum system.

Review of Literature

Early investigators of molybdenum steels found that molybdenum lowered the Ar_1 point. Swinden (1) and later French (2), who confirmed the former work, reported that if the initial heating temperature had not exceeded a certain "lowering" temperature, normal critical points were found on cooling regardless of the rate of heating or time of soaking.[2] If this "lowering" temperature had been exceeded, the normal Ar_1 point was lowered or split, and as the initial heating temperature was increased, the critical point assumed a definite low position.

More recently, Murakami and Takei (3) concluded from their work that the lowering of the critical points of molybdenum steels depended on the following factors:

(1) Carbon concentration
(2) Molybdenum concentration
(3) Maximum heating temperature
(4) Time of soaking
(5) Rate of cooling through the critical region

With steels of constant carbon content, the critical point was lowest in alloys which contained 4.0 to 10 per cent molybdenum. With constant molybdenum content, increasing the carbon content depressed the lowered point until eutectoid carbon concentration was reached; beyond this carbon concentration the lowered point was raised again. The required maximum heating temperature and time of soaking also depended on the chemical composition of the material.

Murakami and Takei stated that the more rapid the cooling rate through the critical range, the more the lowered point was depressed. If the steel were cooled very slowly through the critical range, no lowering was observed. They asserted that in a molybdenum steel whose critical points had been lowered, an acicular ferrite was formed

[2]Extended soaking at high temperature did produce a very slight effect.

which was not present in steels whose critical points had not been lowered.

Takei (4), in his investigation of the iron-carbon-molybdenum system, found that the temperature of the beginning of the Ac_1 transformation was almost constant as the molybdenum content of the alloy increased, but the temperature of the end point was generally higher.

The influence of molybdenum on the carbon content of the iron-carbon eutectoid was studied by Reed (5) who prepared iron-carbon alloys to which he added molybdenum in various amounts. These steels were cooled very slowly to approximate equilibrium conditions and were examined microscopically to determine the eutectoid compositions.

Reed reported that the addition of molybdenum progressively lowered the carbon content required for the eutectoid. With 1.10 per cent molybdenum the carbon concentration of the eutectoid was 0.80 per cent, while only 0.20 per cent carbon was needed if the steel contained 5.10 per cent molybdenum. The results of Reed's work, along with those of Swinden (6) are compared in a diagram by Gregg (7).

The diagrams of Takei (4) and similar ones by Svechnikov and Alferova (8) do not confirm the work of Reed and Swinden. Svechnikov and Alferova state that the eutectoid point shifts very slightly to the left under the influence of increasing molybdenum content, but at 2.5 per cent molybdenum it is again at 0.90 per cent carbon. Thereafter a considerable shifting of this point toward higher carbon concentration takes place.

The existence of a double carbide of iron and molybdenum was not acknowledged by Swinden (1), contrary to the opinion of Guillet (9), who previously had constructed a diagram which distinguished the pearlitic molybdenum steels from the double carbide molybdenum steels. Later, Read and Arnold (10) analyzed carbide residues of high molybdenum steels to determine their chemical composition. They confirmed Guillet's advocation of the formation of a double carbide of iron and molybdenum and offered the formula Fe_3Mo_3C or possibly $Fe_6Mo_6C_2$ as the probable representation of its chemical composition. These investigators prepared a graph to show the relative amounts of Fe_3C and Fe_3Mo_3C in steels with increasing amounts of molybdenum. With an increase of molybdenum concentration the percentages of Fe_3C were shown to diminish and at 18.25 per cent molybdenum the free Fe_3C had completely disappeared.

Gregg (7), in a report of unpublished work by Lester, stated that the double carbide forms preferentially to the iron carbide.

Takei (4), in his investigation of the iron-carbon-molybdenum system, verified the double carbide analyses of Read and Arnold. He constructed an iron-carbon-molybdenum equilibrium diagram

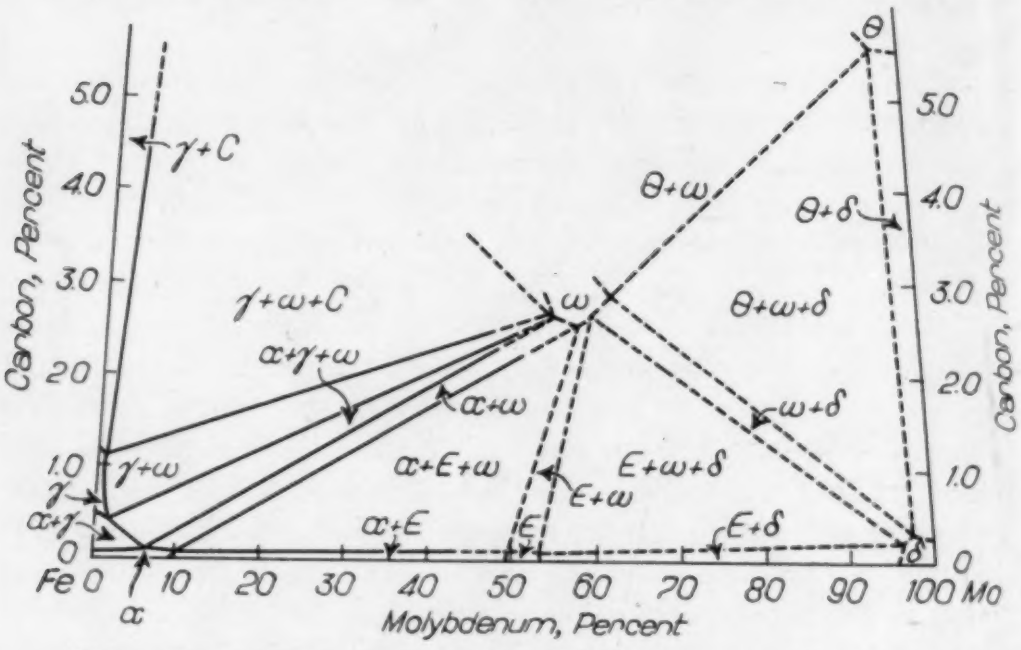


Fig. 1—Section at 1470 Degrees Fahr. (800 Degrees Cent.) of the Iron-Carbon-Molybdenum Equilibrium Diagram Proposed by Takei.

from the results of his thermal, dilatometric, magnetic and microscopic observations. In Fig. 1 the section at 1470 degrees Fahr. (800 degrees Cent.) of the Fe-C-Mo equilibrium diagram, determined by Takei, is reproduced.

The iron-rich sections of the ternary system presented by Takei are distinguished from the Fe-Fe_3C system chiefly by the presence of a double carbide of iron and molybdenum, designated omega phase. The omega phase is formed by the reaction

$$\text{Melt} + Mo_2C = \text{omega}$$

and can be detected in the microstructure by either of two etchants, the Murakami reagent, used by Takei, or the Yatsevich reagent,[3] used by Svechnikof and Alferova. These reagents color the omega phase and leave the Fe_3C unattacked, whereas sodium picrate, which is used to darken Fe_3C, also darkens the double carbide.

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[3]The Yatsevich etch prepared as follows was used in the present investigation for identification of the omega phase: 100 ml H_2O + 10 g Na_2O_2 + 30 ml 30 per cent H_2O_2.

The microstructures of molybdenum steels have been reported by various investigators to be not much different from those of plain carbon steels. Takei (4) stated that the martensite formed in the ternary system was very similar to that obtained in the binary system Fe-Fe_3C. Swinden (1), (6) described the structures observed in his molybdenum steels (carbon 0.20 to 1.15 per cent; molybdenum 1 to 8 per cent) after various heat treatments. With steels in the as-rolled condition "the pearlite was very sorbitic and the structure was very fine." The annealing treatment " 'concentrated' the pearlite." Very fine pearlite was observed in the normalized specimens. The hardened steels in all instances consisted of a "ground mass of martensite—very pale for the mild steels but fairly dark for the hard steels." Tempering "converted martensite into dense troostite" and in some cases "the troostite was intermingled with very fine pearlite."

Rees (11) studied the structure and physical properties of two 0.09 per cent carbon steels which contained 3.95 per cent molybdenum and 6.0 per cent molybdenum. In these molybdenum alloys the ferrite which formed the ground mass of the structure after quenching at 1830 degrees Fahr. (1000 degrees Cent.) was said to have contained Fe_3Mo_2 and Fe_3C in solution.

After quenching from 1470 degrees Fahr. (800 degrees Cent.) the microstructure of the two steels showed a coalescence of carbide which gave rise to a minimum hardness. After a quench from 1830 degrees Fahr. the 3.95 per cent molybdenum steel consisted of martensite and molybdenum ferrite, and the structure of the 6 per cent molybdenum sample contained these constituents plus particles of Fe_3Mo_2 at the grain boundaries and scattered throughout the grains.

Svechnikov and Alferova (8) investigated the steel corner of the iron-carbon-molybdenum system by means of dilatometric, thermal, magnetic and microscopic analyses. The sections of the ternary diagram which they present are reasonably similar to Takei's diagrams for that part of the system.

In alloys containing 2.5 per cent molybdenum and more, sections of a special structure were observed together with a plate-like eutectoid structure resembling pearlite and surrounding the latter. In this structure the plate-like components, different from pearlite, intersected each other with the formation of figures resembling a Widmanstätten structure. This same structural component was observed previously in chromium-molybdenum and copper-molybdenum steels.

Procedure

Forty-one iron-carbon-molybdenum alloys low in sulphur and phosphorus, and containing manganese and silicon in amounts sufficient to produce a killed heat, were used in this investigation. These alloys are grouped roughly into six carbon series, 0.05, 0.20, 0.40, 0.65, 0.85 and 1.20 per cent carbon; each carbon series is composed of alloys with molybdenum ranging from 0.0 to 6.0 per cent molybdenum (approximately).

The alloys were melted in an acid lined, 30-pound high frequency induction furnace. No aluminum additions were made. The ingots were forged into 1-inch round bars and ground to ¾-inch round. The bars were cut into 1⅛-inch long specimens which were nor-

Table I
Chemical Composition of Alloys

Per Cent			
Carbon	Molybdenum	Manganese	Silicon
0.05	0.04	0.14	0.07
0.05	0.39	0.14	0.08
0.05	0.80	0.11	0.07
0.05	1.55	0.11	0.10
0.05	3.17	0.15	0.13
0.05	5.93	0.12	0.07
0.24	0.03	0.17	0.15
0.19	0.20	0.14	0.10
0.29	0.42	0.16	0.14
0.29	0.81	0.15	0.17
0.17	1.49	0.15	0.12
0.19	3.09	0.14	0.11
0.19	5.80	0.14	0.10
0.40	0.02	0.19	0.14
0.45	0.20	0.21	0.19
0.40	0.40	0.18	0.13
0.38	0.78	0.16	0.14
0.38	1.70	0.16	0.15
0.37	3.17	0.17	0.11
0.39	5.74	0.18	0.14
0.81	0.02	0.18	0.12
0.66	0.20	0.18	0.13
0.58	0.40	0.15	0.14
0.67	0.88	0.19	0.16
0.78	1.63	0.31	0.18
0.80	3.16	0.26	0.18
0.68	5.86	0.22	0.14
0.87	0.02	0.17	0.19
0.88	0.20	0.21	0.19
0.95	0.40	0.21	0.10
0.89	0.79	0.28	0.18
0.85	1.59	0.17	0.15
0.86	3.17	0.20	0.15
0.88	6.34	0.15	0.13
1.20	0.02	0.28	0.20
1.15	0.22	0.26	0.18
1.14	0.45	0.23	0.33
1.12	0.76	0.23	0.31
1.12	1.62	0.19	0.12
1.10	3.11	0.19	0.18
1.33	6.07	0.20	0.07

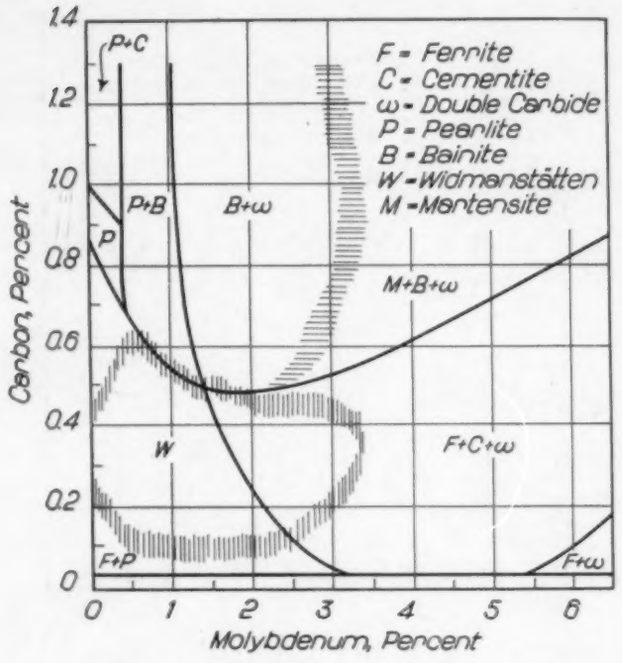


Fig. 2—Constitution Diagram, 1850 Degrees Fahr. Air-Cooled.

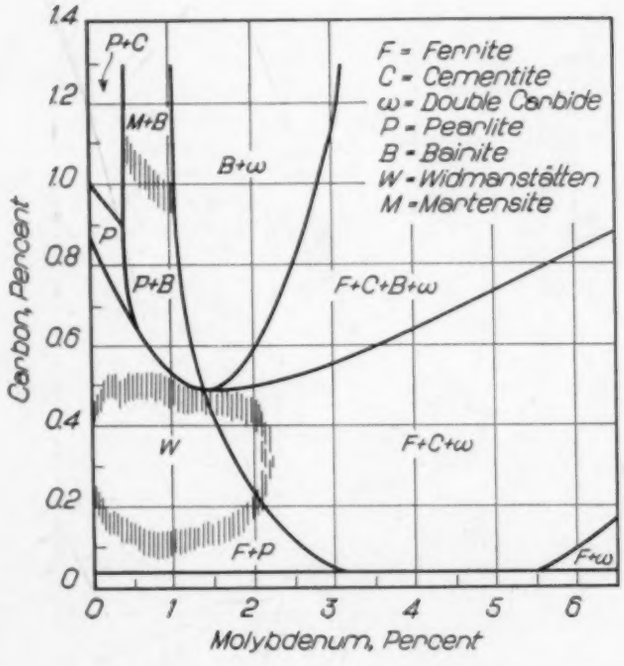


Fig. 3—Constitution Diagram, 1750 Degrees Fahr. Air-Cooled.

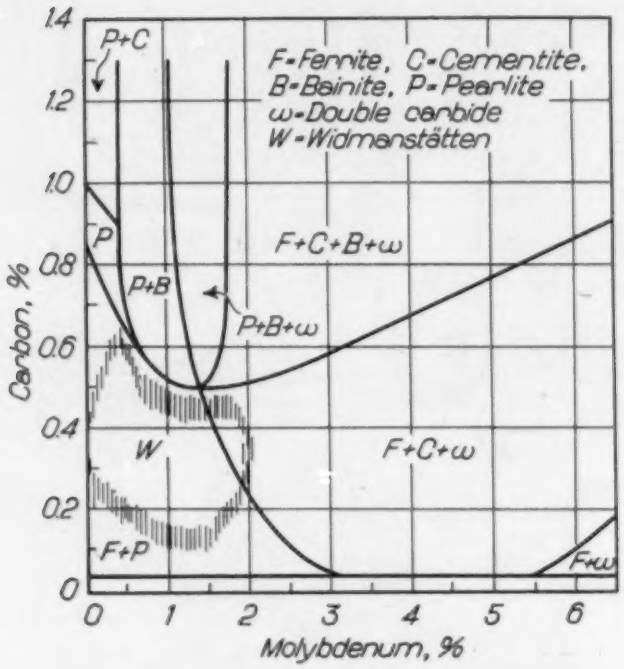


Fig. 4—Constitution Diagram, 1650 Degrees Fahr. Air-Cooled.

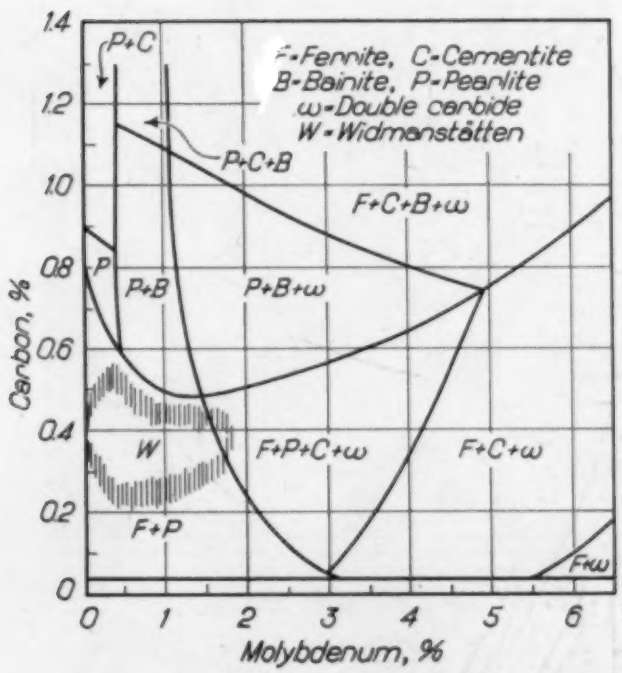


Fig. 5—Constitution Diagram, 1550 Degrees Fahr. Air-Cooled.

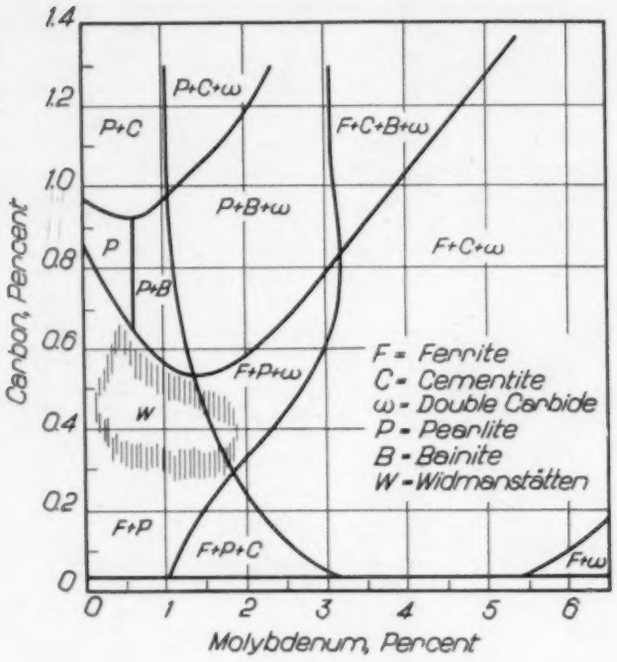


Fig. 6—Constitution Diagram, 1450 Degrees Fahr. Air-Cooled.

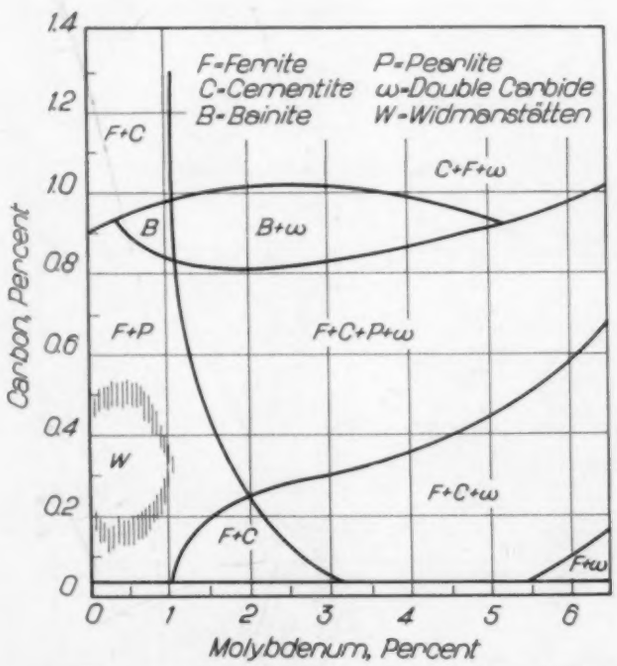


Fig. 7—Constitution Diagram, 1350 Degrees Fahr. Air-Cooled.

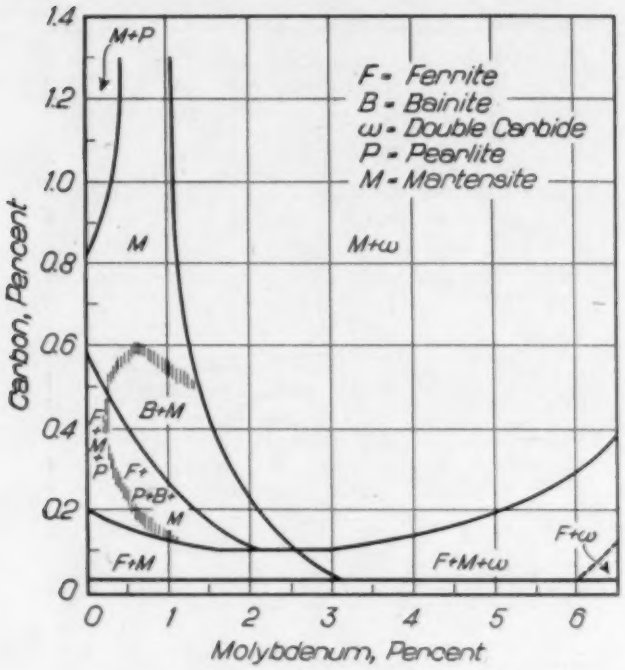


Fig. 8—Constitution Diagram, 1850 Degrees Fahr. Water-Quenched.

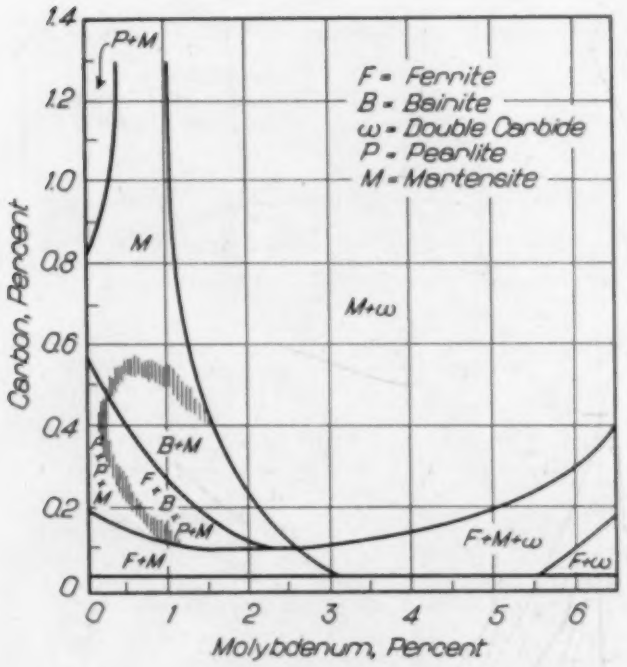


Fig. 9—Constitution Diagram, 1750 Degrees Fahr. Water-Quenched.

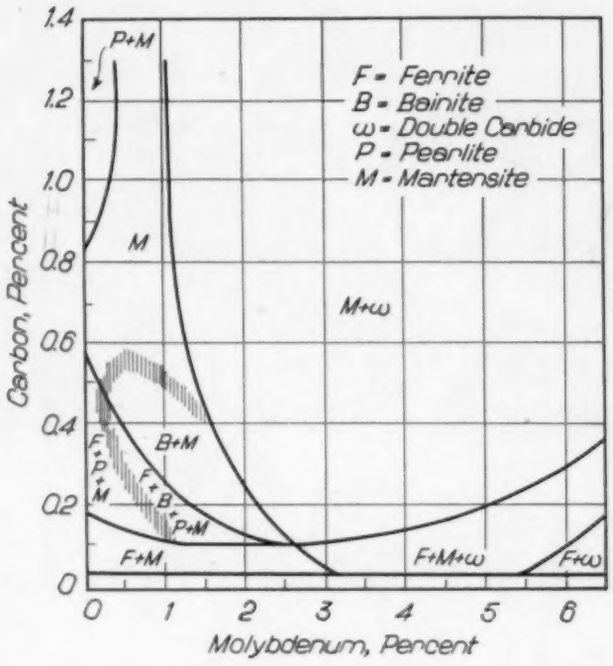


Fig. 10—Constitution Diagram, 1650 Degrees Fahr. Water-Quenched.

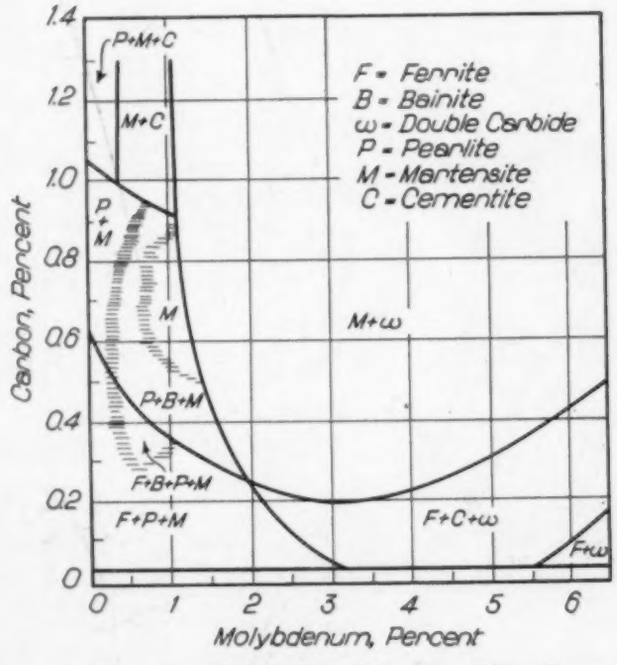


Fig. 11—Constitution Diagram, 1550 Degrees Fahr. Water-Quenched.

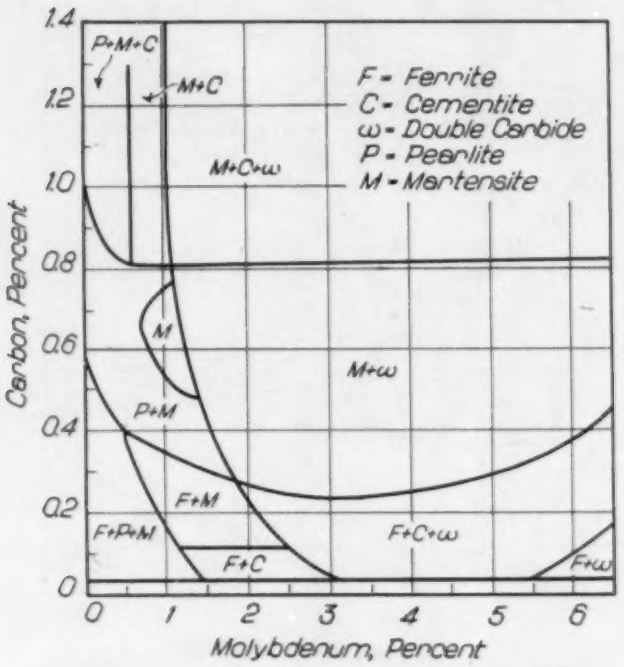


Fig. 12—Constitution Diagram, 1450 Degrees Fahr. Water-Quenched.

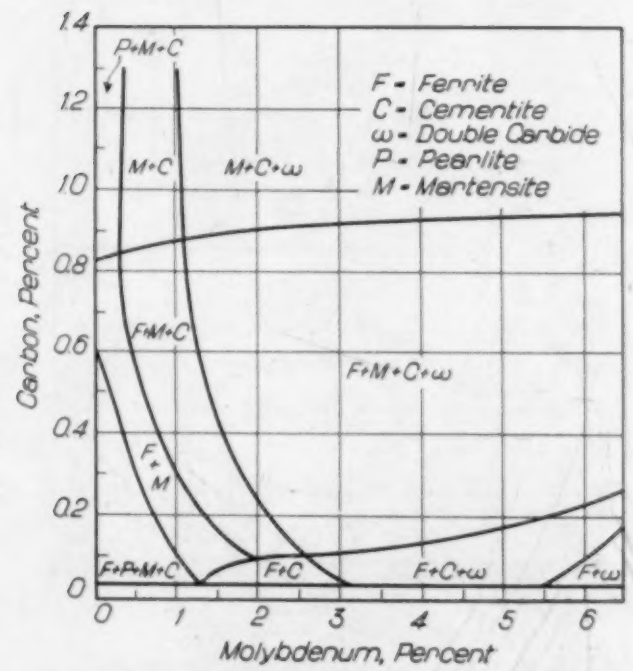


Fig. 13—Constitution Diagram, 1350 Degrees Fahr. Water-Quenched.

Table II

Hardness of Iron-Carbon-Molybdenum Alloys Quenched in Water—Rockwell "C" Scale

		Quenching Temperature—Degrees Fahr.					
C	Mo	1350	1450	1550	1650	1750	1850
0.05	0.04	10	6	2	2	1	2
....	....	..	..	..	..	..	..
0.05	0.39	10	8	1	7	10	5
0.05	0.80	12	8	4	8	10	7
0.05	1.55	−4	6	1	5	16	18
0.05	3.17	−4	−3	−1	7	12	15
0.05	5.93	−4	−5	−4	−4	−1	4
0.24	0.03	6	17	18	26	34	33
0.19	0.20	8	17	15	19	17	28
0.29	0.42	12	35	33	32	42	43
0.29	0.81	11	37	46	44	42	44
0.17	1.49	16	22	32	41	38	39
0.19	3.09	25	22	22	40	44	43
0.19	5.80	3	3	4	15	27	38
0.40	0.02	23	27	29	31	40	25
0.45	0.20	30	47	40	44	46	48
0.40	0.40	30	51	45	43	44	49
0.38	0.78	25	51	44	45	44	49
0.38	1.70	32	48	41	44	48	52
0.37	3.17	33	40	44	44	47	50
0.39	5.74	29	31	37	44	48	50
0.81	0.02	45	52	45	51	52	55
0.66	0.20	48	50	47	49	51	52
0.58	0.40	43	46	47	50	52	52
0.67	0.88	46	53	52	53	53	55
0.78	1.63	52	56	54	55	56	57
0.80	3.16	53	52	55	56	59	59
0.68	5.86	44	54	53	54	57	57
0.87	0.02	43	55	54	56	62	58
0.88	0.20	54	58	56	57	58	60
0.95	0.40	57	57	55	62	57	62
0.89	0.79	47	57	54	59	57	62
0.85	1.59	43	58	57	59	58	63
0.86	3.17	44	59	58	60	59	61
0.88	6.34	52	59	57	60	60	62
1.20	0.02	41	48	52	54	62	60
1.15	0.22	50	55	62	55	63	60
1.14	0.45	59	61	58	57	65	56
1.12	0.76	61	62	60	59	62	59
1.12	1.62	59	62	61	61	61	59
1.10	3.11	63	61	62	62	62	60
1.33	6.07	64	63	65	60	65	61

malized at 1800 degrees Fahr. (980 degrees Cent.) and sandblasted to remove scale prior to heat treatment. Twelve heat treatments were used—a water quench and an air cool in still air from 1350, 1450, 1550, 1650, 1750 and 1850 degrees Fahr. (735, 790, 845, 900, 955 and 1010 degrees Cent.). Each specimen was cut into two pieces ½ inch long for microscopic work and hardness measurements. In all cases the hardness and microstructures were taken at a point equidistant from the center and the cylindrical surface of the specimens.

Table I gives the chemical composition of the alloys. The hardnesses of each of the alloys after each heat treatment are given in Tables II and III. In Figs. 2 to 13 the constitution diagrams are presented. (A chart showing the distribution of the alloys according to composition is given in Fig. 23.)

The boundaries which enclose the compositions having the same structural types were located by estimation of the relative amounts of each micro-constituent and while not precisely determined can be regarded as reasonably accurate. The diagrams are therefore considered to give a useful picture of the structural changes which take place in this system as a result of the heating temperatures and the cooling rates used.

Microstructure

In examining the microstructures of the alloys, the following constituents were recognized:

1. Ferrite
2. Pearlite
3. Bainite
4. Martensite
5. Carbide (of cementite type)
6. Double carbide of iron and molybdenum (omega)

Where the treatment resulted in the formation of the Widmanstätten pattern, this was also noted in the constitution diagrams.

Omega Phase

The only phase appearing in these alloys which is not possible in iron-carbon alloys is the double carbide of iron and molybdenum. This phase was identified in all the specimens containing 1.5 per cent or more molybdenum with the exception of those containing only 0.20 and 0.05 per cent carbon. As indicated in the diagrams, the double carbide or omega phase will appear in alloys with only slightly more than 1 per cent molybdenum when the carbon content is above the eutectoid composition. The typical appearance of the omega phase is illustrated in Fig. 14 where omega (white) is associated with martensite (matrix). In Fig. 15 the omega phase is embedded in ferrite and at the grain boundaries. In lower molybdenum specimens where lesser amounts of the double carbide occur it is necessary to use the Yatsevich etch (or Murakami reagent) for positive identification of this phase.

Widmanstätten Structure

In the constitution diagrams for the normalized condition, areas marked "W" (Widmanstätten) will be found. Fig. 16 shows the structure so named. The authors are unable to identify the dark areas as fine lamellar pearlite, which is the common interpretation of

Table III
Hardness of Iron-Carbon-Molybdenum Alloys Normalized—Rockwell "C" Scale

		Normalizing Temperature—Degrees Fahr.					
C	Mo	1350	1450	1550	1650	1750	1850
0.05	0.04	−20	−16	−20	−22	−18	−20
....	....	..	..	..	..	..	..
0.05	0.39	−12	−7	−10	−12	−9	−12
0.05	0.80	−10	−6	−4	−9	−6	−5
0.05	1.55	−8	−2	−3	−5	−5	−6
0.05	3.17	−7	−8	−10	−4	−5	−4
0.05	5.93	−5	−6	−9	−7	−5	−1
0.24	0.03	−15	−12	−6	−6	−6	−8
0.29	0.20	−15	−14	−10	−10	−8	−7
0.29	0.42	−1	3	8	8	10	11
0.29	0.81	7	9	17	17	18	17
0.17	1.49	14	10	5	16	19	20
0.19	3.09	23	19	7	12	13	31
0.19	5.80	4	0	−1	4	5	10
0.40	0.02	−2	2	2	3	3	3
0.45	0.20	4	11	12	14	14	15
0.40	0.40	8	14	14	14	14	14
0.38	0.78	11	17	18	20	19	18
0.38	1.70	18	17	25	26	27	26
0.37	3.17	24	17	18	30	32	33
0.39	5.74	25	17	17	18	32	36
0.81	0.02	18	25	26	27	27	28
0.66	0.20	17	23	23	24	24	25
0.58	0.40	16	22	18	23	23	23
0.67	0.88	22	30	32	33	32	32
0.78	1.63	28	33	34	39	43	43
0.80	3.16	30	34	35	39	44	53
0.68	5.86	28	34	33	35	38	39
0.87	0.02	15	27	29	28	29	29
0.88	0.20	16	30	33	34	34	34
0.95	0.40	17	33	36	37	38	38
0.89	0.79	20	34	37	36	36	37
0.85	1.59	23	33	34	36	38	39
0.86	3.17	25	36	36	37	40	44
0.88	6.34	25	36	36	37	39	42
1.20	0.02	16	23	29	30	35	35
1.15	0.22	15	23	31	40	40	40
1.14	0.45	25	32	38	43	43	42
1.12	0.76	29	35	39	42	55	45
1.12	1.62	30	36	38	40	43	46
1.10	3.11	33	39	39	39	42	59
1.33	6.07	34	39	40	40	42	46

this constituent. Even observation at high magnification (× 1500, oil immersion) disclosed no lamellar structure and, to be strictly accurate, ferrite and carbide is suggested as a truer identification. The carbide may be in sub-microscopic lamellae or in fine spheroids, more probably the latter.

Martensite

In examining the series of quenched structures in this system it is observed that the martensitic needles become smaller as the molybdenum content increases, somewhat paralleling the austenitic grain size. At high molybdenum content the familiar acicular structure is not much in evidence unless the carbon content is also very high. The martensite in Fig. 17 (1.33 per cent carbon, 6.07 per cent molyb-

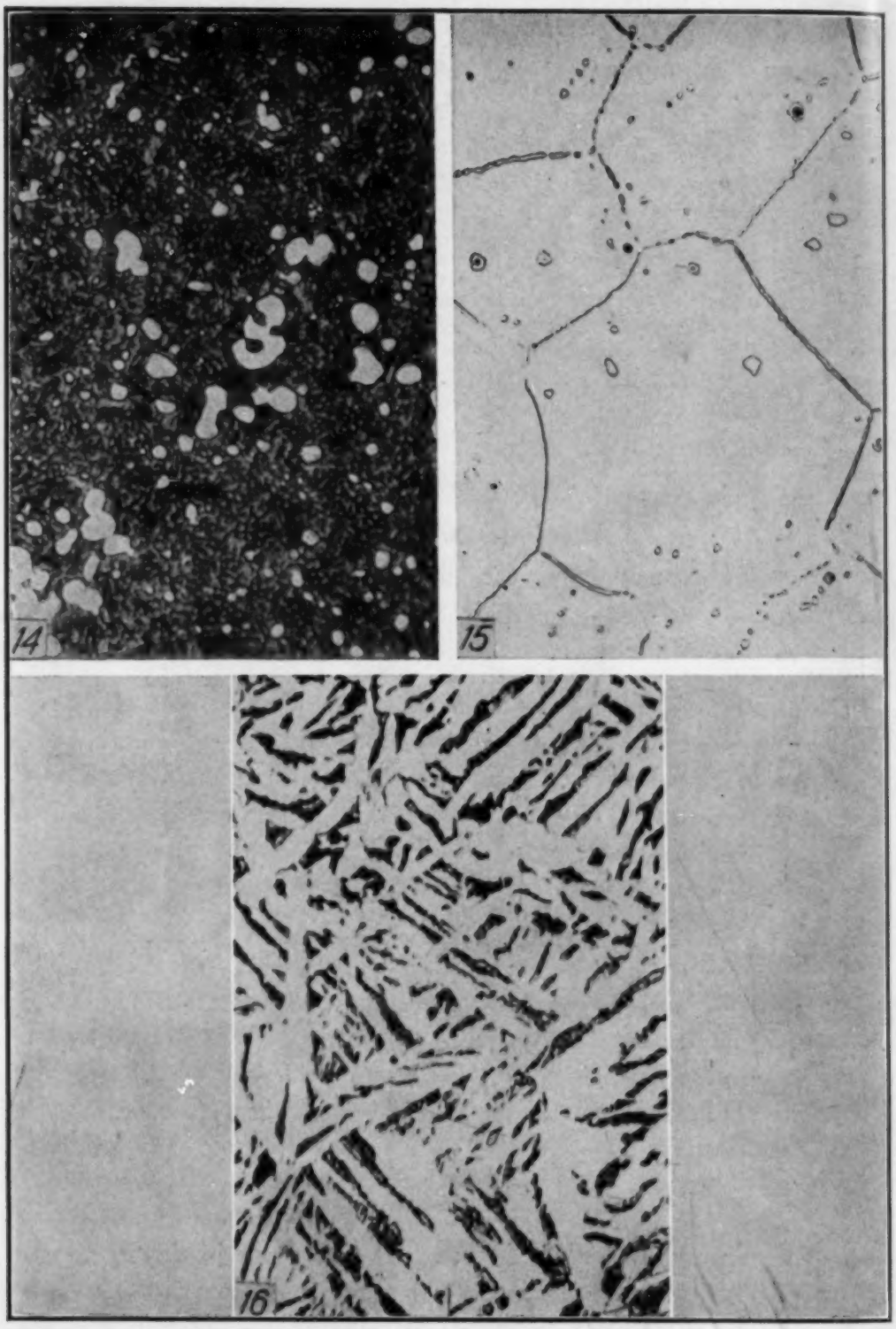


Fig. 14—Alloy Containing 0.68 Per Cent Carbon, 5.86 Per Cent Molybdenum, Water-Quenched from 1650 Degrees Fahr., Showing Omega Phase in Granular Martensite. Etched in 2 Per Cent Nital. × 1500.

Fig. 15—Alloy Containing 0.05 Per Cent Carbon, 5.93 Per Cent Molybdenum, Normalized from 1450 Degrees Fahr., Showing Ferrite and Omega Phase. Etched in 2 Per Cent Nital. × 500.

Fig. 16—Alloy Containing 0.29 Per Cent Carbon, 0.42 Per Cent Molybdenum, Normalized from 1850 Degrees Fahr., Showing Typical Widmanstätten Structure. Etched in 2 Per Cent Nital. × 500.

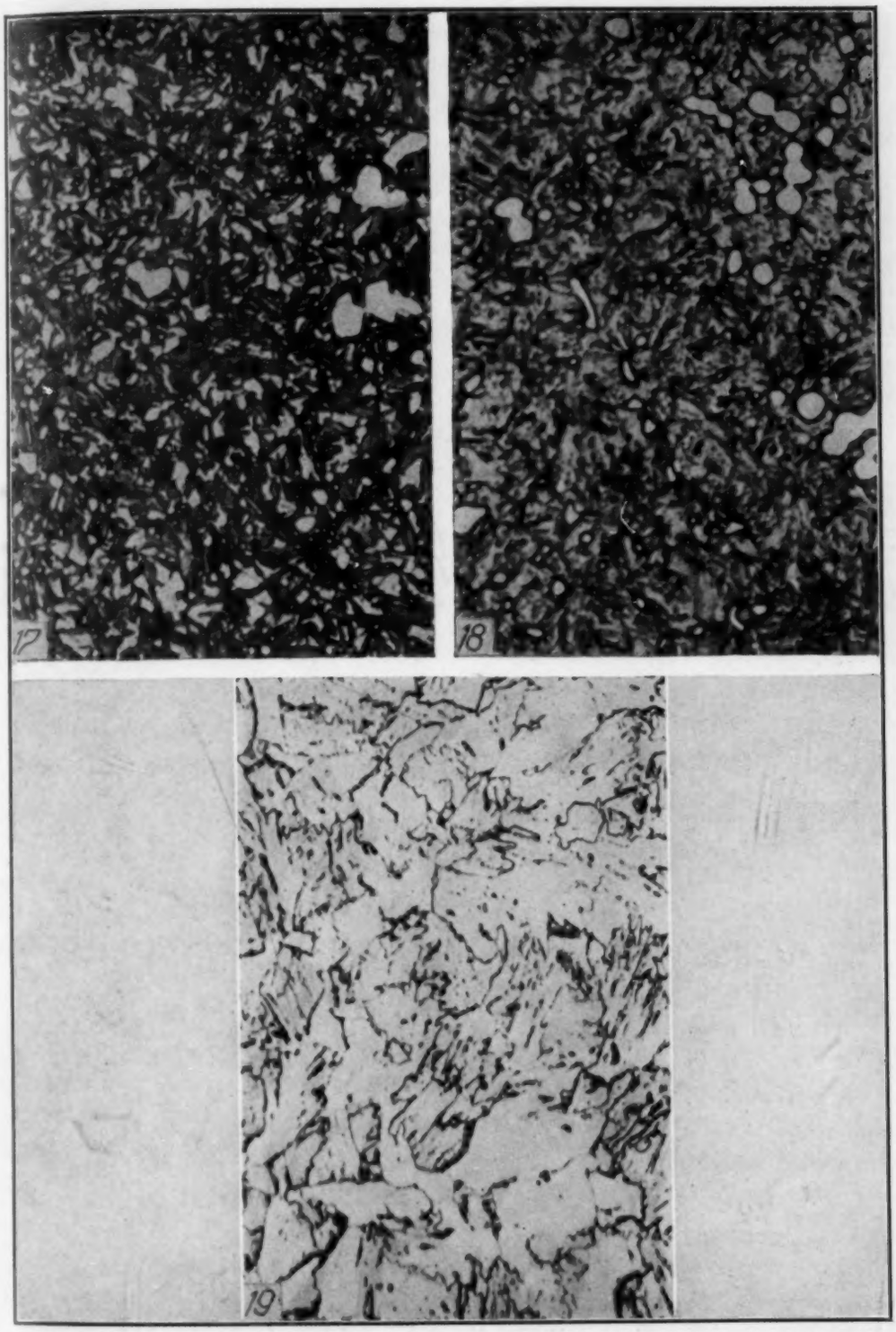


Fig. 17—Alloy Containing 1.33 Per Cent Carbon, 6.0 Per Cent Molybdenum, Water-Quenched from 1750 Degrees Fahr., Showing High Molybdenum Martensite. Etched in 2 Per Cent Nital. × 1500.

Fig. 18—Alloy Containing 0.88 Per Cent Carbon, 6.34 Per Cent Molybdenum, Water-Quenched from 1850 Degrees Fahr., Showing Modified Martensite. Etched in 2 Per Cent Nital. × 1500.

Fig. 19—Alloy Containing 0.05 Per Cent Carbon, 0.39 Per Cent Molybdenum, Water-Quenched from 1750 Degrees Fahr., Showing Low Carbon Martensite. Etched in 2 Per Cent Nital. × 500.

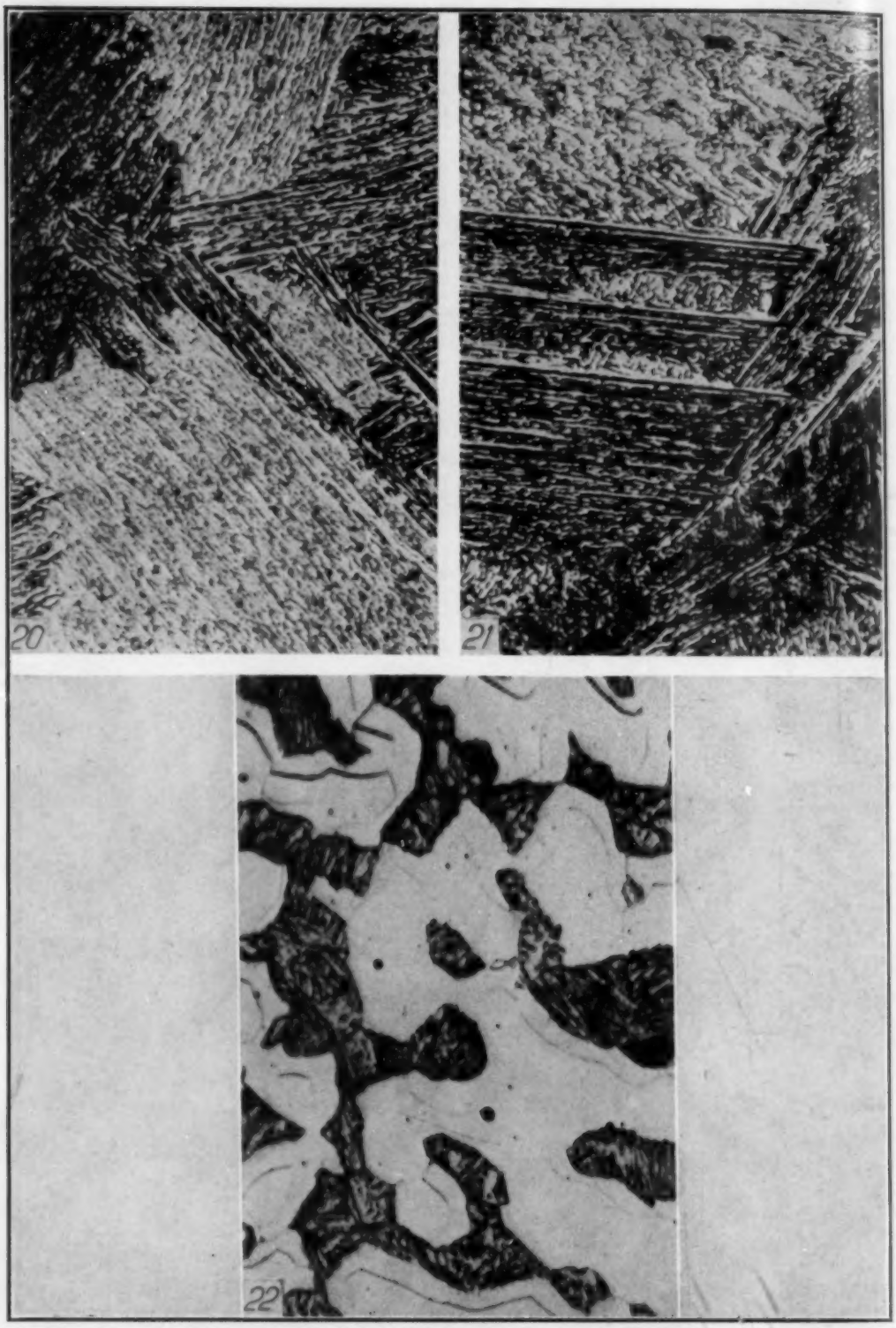


Fig. 20—Alloy Containing 0.89 Per Cent Carbon, 0.79 Per Cent Molybdenum, Normalized from 1750 Degrees Fahr., Showing Bainite. Etched in 4 Per Cent Picral. × 1000.

Fig. 21—Alloy Containing 0.89 Per Cent Carbon, 0.79 Per Cent Molybdenum, Normalized from 1850 Degrees Fahr., Showing Bainite. Etched in 4 Per Cent Picral. × 1000.

Fig. 22—Alloy Containing 0.05 Per Cent Carbon, 3.17 Per Cent Molybdenum, Water-Quenched from 1850 Degrees Fahr., Showing Two Ferrite Phases of Different Origins. Etched in 2 Per Cent Nital. × 500.

denum), while yet acicular, is much finer than plain carbon martensite. Fig. 18 (0.88 per cent carbon, 6.34 per cent molybdenum) reveals more definitely the modification which is operating and in the extreme case, Fig. 14 (0.68 per cent carbon, 5.86 per cent molybdenum), the martensite appears almost as a granular rather than acicular matrix, as in high speed steel, quenched from too low a temperature and heavily etched.

The effect of lower molybdenum contents on the structure of low carbon martensite is not apparent, as may be seen in Fig. 19 (0.05 per cent carbon, 0.39 per cent molybdenum).

Bainite

That bainite was produced at all in these alloys by conventional heat treatment might be regarded as unusual in consideration of the form of the transformation curve (so-called "S-curve") for plain carbon steels. That it can occur as a result of molybdenum content is evidenced by the fact that areas consisting almost entirely of this constituent were located. Figs. 20 and 21 are presented as illustrations.

The presence of bainite in appreciable amounts indicates that the addition of molybdenum brings about significant changes in the shape of the transformation curves. The nature and extent of these changes are already being investigated by the authors and by others, and it has been found that in certain alloy steels the slow transformation rate at higher temperatures distorts the "S-curve" far to the right, and that a moderate cooling rate is adapted to cause transformations above the temperature for martensite. The distinction between the constituent bainite and the constituent martensite is inherently not so clear cut as it appears in a comparison of Figs. 21 and 17. For this reason, this transition is indicated in the diagrams by shaded areas. The distinction between bainite and pearlite, however, is marked and can be readily made as soon as one has had the opportunity to examine several typical structures.

Pearlite

In the study of the structures no apparent change in the manifestation of pearlite was noticed as a result of the content of molybdenum. Obviously both the amount of pearlite and its lamellar spac-

ing change as the rate and temperature of transformation are varied by molybdenum additions. However, when once formed, nothing characteristic of the molybdenum content could be detected in this constituent.

Ferrite

The only interesting point in connection with the occurrence of this phase in these alloys is illustrated in Fig. 22. This structure, consisting of ferrite, martensite and omega, shows boundaries in the

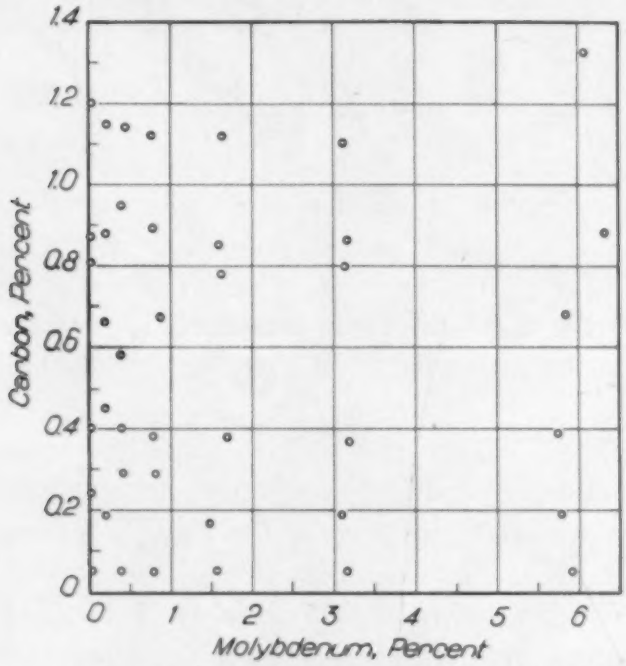


Fig. 23—Chart Showing Distribution of Analyses of the 41 Iron-Carbon-Molybdenum Alloys.

ferrite concentric with the martensitic areas. The areas adjacent to the martensite are pro-eutectoid ferrite. The remaining ferrite is that which did not transform to austenite at the temperature of heating prior to quenching.

Carbide of Cementite Type

While this carbide phase probably contains molybdenum in solution, the amounts are not known and any difference in etching characteristics from pure cementite was imperceptible.

Summary

1. Forty-one Fe-C-Mo alloys ranging in composition from 0.05

to 1.2 per cent carbon and 0 to 6.0 per cent molybdenum were prepared.

2. The structural characteristics and hardnesses of these alloys were determined both in the quenched and in the normalized conditions, using temperatures from 1350 to 1850 degrees Fahr. in 100-degree-Fahr. intervals.
3. Constitution diagrams were constructed on the basis of the observations made.

Conclusion

Structurally, the primary effect of molybdenum appears to be one of restriction of austenite grain growth, or refinement when acting in the presence of carbon. That its presence when dissolved in austenite produces important changes on the rate of transformation curves is indicated by the frequent and extensive occurrence of the direct transformation product, bainite. It strongly retards the transformation of austenite, thereby inducing high hardenability.

The authors believe that temperature-dilation curves of molybdenum steels, showing split criticals, are simply the recording of the proportionate transformations occurring at two different points on the "S-curve." A moderate shift of the nose of the "S-curve" to the right always results in an apparent lowering of the critical point.

The omega phase appears to be well established and its occurrence in commercial molybdenum steels containing more than 1.5 per cent molybdenum cannot be questioned.

This work points out the desirability of more careful study of the solubility of molybdenum in Fe_3C, and especially the shift of the A_{cm} line due to molybdenum. The authors propose a study of these points in a continuation of this work.

Acknowledgment

The authors desire to express their indebtedness to Dr. E. C. Bain and E. S. Davenport for their criticisms and counsel throughout the investigation and in the construction of the constitution diagrams.

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HARDNESS GRADIENTS IN TEMPERED STEEL CYLINDERS

By C. A. Rowe and R. A. Ragatz

Abstract

Curves are presented which show the hardness gradients in 1-inch diameter cylinders after quenching and after tempering. Results are shown for nine different plain carbon steels varying in carbon content from 0.17 to 1.20 per cent, and for tempering temperatures ranging from 400 to 1275 degrees Fahr. Photomicrographs for three typical steels show a close correlation between the structural changes observed and the results of the hardness surveys.

Introduction

THE numerous investigations on the hardenability of steel which have been carried out in recent years have resulted in the publication of many graphs showing hardness gradients in quenched steel cylinders. Such studies appear to have been confined almost exclusively to specimens in the "as-quenched" state. It was felt that results of interest and value would be obtained by making a study of the hardness variations existing in steel cylinders that were tempered after quenching. This paper presents the results of such an investigation.

The selection of a sufficiently large section diameter for cylindrical specimens will result in incomplete hardening on quenching. An outer shell of hard martensite will form, surrounding an inner core of much softer "fine pearlite" (primary troostite), with an intervening transition zone containing both constituents. If specimens of such character are subjected to various tempering treatments, a hardness survey across the section will reveal the effect that a given tempering treatment will have on martensite and "fine pearlite" of identical composition.

It was anticipated that the relative hardness changes exhibited

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by the shell and core might provide some evidence regarding the structural identity or nonidentity of primary and secondary troostite. If it is postulated that the decomposition products of martensite are structurally identical with primary troostite, it would follow that entirely flat hardness traverse curves should be obtained on tempering at temperatures above that necessary to reduce shell and core to identical hardness. If, however, the experimental results show a differential of hardness between shell and core for those tempering temperatures that lie above that needed to bring shell and core to identical hardness, then the hypothesis that primary and secondary troostite are structurally identical is hardly tenable.

It is realized that the work of Lucas on the microstructure of primary troostite at high magnifications and the work of Bain and associates on the transformation of austenite at subcritical temperatures have led to the quite general, though not universal, acceptance of the lamellar character of primary troostite and of the spheroidal character of the decomposition products of martensite. However, it was felt that some additional evidence deduced from hardness surveys would be an interesting by-product of the present investigation.

Experimental Method

The Steels Used—Nine plain carbon steels varying from 0.17 to 1.20 per cent carbon were employed in this investigation. The composition and history of the various steels, as fully as known, are recorded in Table I. The six steels varying from 0.17 to 0.86 per cent carbon were hot-rolled basic open-hearth steel, and were received in the pearlitic state. The steel of lowest carbon content, (0.17 per cent) was evidently a rimmed steel, as the etched cross section exhibited an approximately rectangular core of segregated material which occupied the greater part of the cross section. The three steels of highest carbon content, (0.88 to 1.20 per cent), were annealed carbon tool steel, and exhibited the usual spheroidal structure when examined microscopically. Steels SR96 and 97 have approximately the same composition, but the former is a deep hardening tool steel while the latter is a shallow hardening tool steel. The three tool steels were made in the basic electric furnace and were hot-rolled to shape. All materials in the investigation proper were used in the "as-received" state, without the application of normalizing or other pre-quench treatments.

In order to ascertain the uniformity of each stock material, Rockwell hardness surveys were made on two samples of each material in the annealed state. As indicated above, the three tool steels were received from the manufacturer in the annealed state, and it was therefore unnecessary to apply any further treatments to these three materials. The other six steels, being in the hot-rolled state

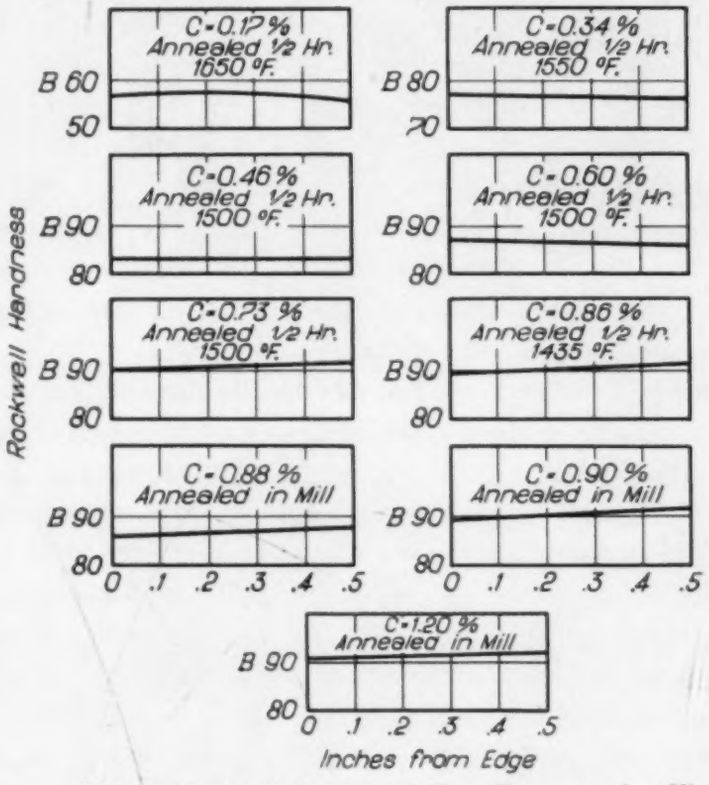


Fig. 1—Averaged Results of Two Traverses for Nine Different Steels.

as supplied by the manufacturer, were annealed in a laboratory furnace, using temperatures in accordance with the recommendations given in the A.S.M. Handbook. The averaged results of the two traverses for each steel are presented in Fig. 1. The curves show only slight variations in hardness from center to surface, indicating that the materials were of sufficient uniformity for the purposes of the present investigation.

Preparation of Specimens for Quenching—Cylinders 1-inch in diameter and 4 inches in length were machined from the "as-received" stock bars and were finished with No. 150 emery cloth. The diameters were held to 0.003 inch. A diameter of 1-inch was considered to be the most suitable for the present investigation. It may be noted that this is in accordance with the recommendation of Burns, Moore,

Table I
Data on Steels Used

Identification Number	C	Mn	P	S	Si	Cr	Ni	Stock Bar Diameter	Quenching Temperature Degrees Fahr.
	Per Cent								
SR87	0.17	0.47	0.010	0.036	....	....	....	1 1/16"	1650
SR92	0.34	0.74	0.025	0.032	....	....	....	1 1/8"	1550
SR89	0.46	0.70	0.015	0.023	....	....	....	1 1/16"	1500
SR85	0.60	0.53	0.018	0.031	....	....	....	1 1/4"	1500
SR84	0.73	0.56	0.018	0.028	0.18	....	....	1 1/2"	1500
SR86	0.86	0.41	0.015	0.032	0.19	....	....	1 1/8"	1435
SR97	0.88	0.25	0.013	0.009	0.12	0.08	0.10	1 1/8"	1425
SR96	0.90	0.30	0.012	0.012	0.22	0.12	0.04	1 1/8"	1425
SR95	1.20	0.34	0.010	0.009	0.22	0.10	0.08	1 1/8"	1425

The first six steels were basic open-hearth, hot-rolled steels with a pearlitic structure. The last three steels were basic electric, hot-rolled, annealed with spheroidal structure.

and Archer[1] that a diameter of 1 inch be used for evaluating the hardenability of plain carbon steels.

Quenching Treatments—An electrically heated muffle furnace was brought to the desired quenching temperature and allowed to regulate at temperature until thermal equilibrium was established within the furnace. Two of the steel cylinders were inserted into the muffle, and supported on refractory wedges. The time was noted when the desired temperature was regained, and the specimens were left in the furnace for one half hour from this noted time. They were then removed and quenched, one at a time, in a tank of 5 per cent lye solution which was kept at 65 to 75 degrees Fahr.

Temperatures were measured and controlled by means of a calibrated 8-gage chromel-alumel thermocouple, connected to a controller-indicator of the millivoltmeter type.

The heat treating procedure as regards temperature and time conforms to the recommendations of the A.S.M. Handbook. The quenching temperatures used are indicated in Table I.

Preparation of Specimens for Tempering—Disks one-fourth inch thick were cut from the hardened steel cylinders, making discards of at least 1 inch from each end of the cylinders. Such discards were found to be sufficient to eliminate end cooling effects.

All cut-off work was done by means of a $\frac{1}{16}$-inch carborundum wheel, with a jet of cold water applied to the wheel directly where the cut was being made. Extreme care was used to prevent the introduction of tempering effects. A proper cut-off procedure was

[1]J. L. Burns, T. L. Moore and R. S. Archer, "Quantitative Hardenability," TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 1-36.

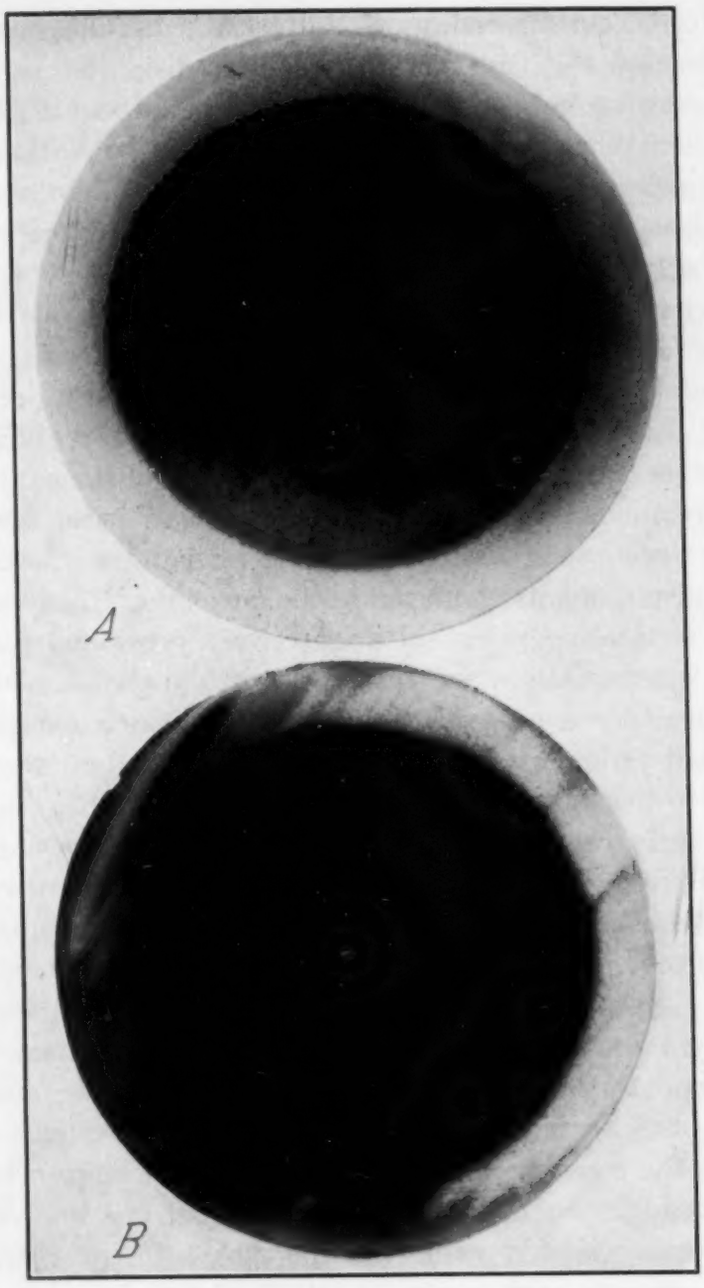


Fig. 2—Polished and Etched Section of "As-Quenched" Material. Upper—Proper Cut-Off Procedure. Lower—Improper Cut-Off Procedure.

worked out through the information gained in examining polished and etched sections after cutting. Even slight tempering from the cut-off operation will give the effect shown in the lower macrograph of Fig. 2. The upper macrograph of Fig. 2 shows the appearance if tempering effects are absent.

After the cut-off operation, a Rockwell hardness traverse was run on one of the flat surfaces of each disk and supplementary readings were taken on the outer cylindrical surfaces. Thus, a hardness gradient curve prior to tempering was established for each individual specimen. For a given steel, these hardness gradient curves when superimposed upon one another showed very satisfactory checks.

Sufficient disks of each kind of steel were cut to provide two specimens for each tempering treatment.

Tempering Treatments—Tempering temperatures of 400, 600, 800, 1000, 1200, and 1275 degrees Fahr. (205, 315, 425, 540, 650, and 690 degrees Cent.) were employed.

All treatments were carried out in a salt bath, heated in an electric furnace which utilized the same temperature measuring and control system that was employed in the quenching treatments. Commercial heat treating salts which effectively prevented scale formation and decarburization were used as bath material. Microscopic examination showed no evidence of decarburization except with the 0.17 per cent carbon steel tempered at the two highest temperatures. The effect in these two instances was extremely slight.

The salt bath was brought up to the desired tempering temperature and allowed to control at temperature for at least one-half hour to insure the establishment of steady state thermal conditions. The disks to be tempered were placed on edge in a wire rack in such a way that no specimens were in contact. The wire rack and contents were lowered into the salt bath. The time was noted when the desired temperature was regained. The specimens were left in the furnace for one hour after this noted time. All specimens were air-cooled after the completion of the tempering treatment. The tempering cycle conforms to Palmer's[2] suggestion that one hour is suitable for most commercial tempering treatments.

After grinding with emery paper, Rockwell hardness traverses were run across one of the flat surfaces of each specimen, taking readings on the surface opposite to that used for the hardness traverses in the "as-quenched" state. Cylindrical surface hardness readings were also taken.

Operation of the Rockwell Hardness Tester—All hardness readings were made with a standard model Rockwell hardness tester. In

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[2]F. R. Palmer, "Tool Steel Simplified," 1937, p. 120.

general, the customary limits of C20 minimum and B100 maximum were observed in taking the hardness data. However, there were some borderline cases where it was necessary to go below C20 or over B100 in making a hardness traverse from surface to center.

In making hardness traverses, it was observed that when the edge of the specimen was approached too closely, the Rockwell reading declined, presumably due to inadequate support of the penetrator on the side towards the edge. Such low hardness readings obviously are of no significance and were rejected.

Due to the fact that readings cannot be taken close to the edge when making a traverse of a flat surface, considerable importance attaches to the readings taken on the outer cylindrical surfaces. The question was raised whether or not the readings taken on the surface of a cylinder 1-inch in diameter could be regarded as true hardness values, the thought being that the curvature might tend to produce low hardness readings. In order to answer this question, flat surfaces approximately $\frac{3}{16}$-inch wide were ground on the cylindrical surfaces of a series of specimens selected to cover the range of hardness values to be encountered in the investigation. A comparison of the hardness readings obtained on the flat surfaces with those taken directly on the cylindrical surfaces showed almost identical checks, both when using the C and B penetrators. These results not only indicate the correctness of readings taken directly on the cylindrical surfaces, but also indicate that decarburization effects are negligible.

In the case of the rimmed steel (SR87, C = 0.17 per cent) it was necessary to polish and etch each specimen in order to orient the central segregated region with respect to the hardness traverses. The diametral traverse lines were run perpendicular to the boundary of the central rectangular core of segregated material.

In making all hardness traverses, the individual impressions were separated sufficiently to prevent error in the readings. The device of staggering the readings, rather than of having all in the same line, was adopted in order to secure more readings.

Results Obtained

Hardness Gradients—In order to show the accuracy of the experimental data, detailed curves are presented in Figs. 3, 4 and 5 for the 0.88 per cent carbon tool steel. It will be observed that very satisfactory checks were obtained between duplicate specimens, and that the individual points line up to give smooth curves.

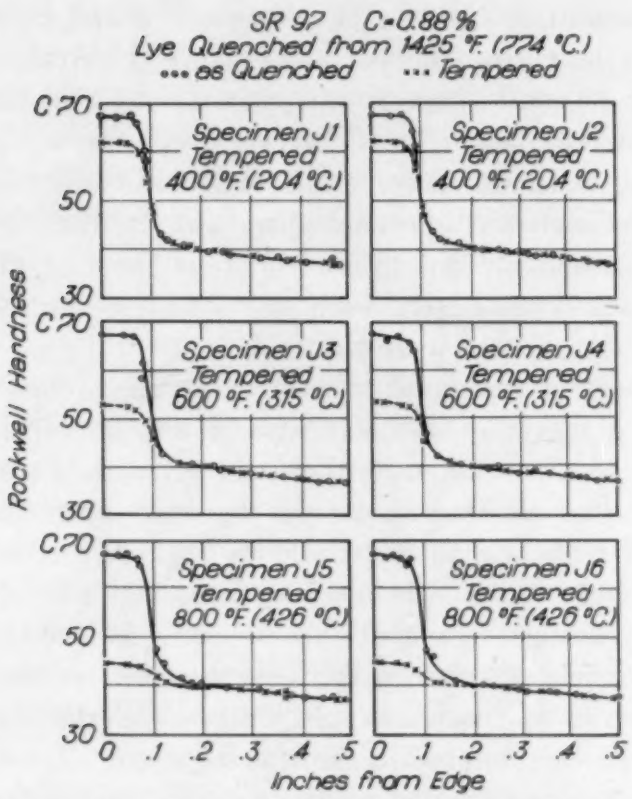


Fig. 3—Steel SR97 Lye Quenched from 1425 Degrees Fahr.

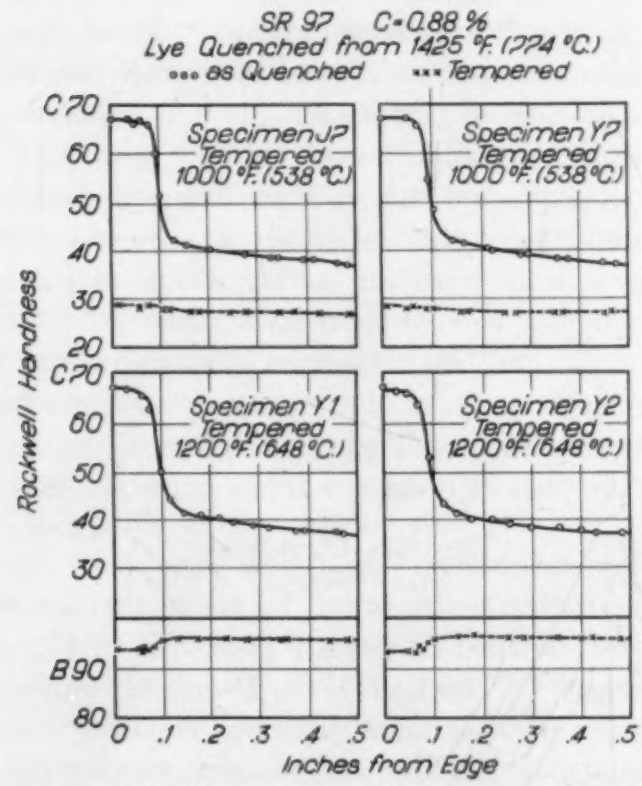


Fig. 4—Steel SR97 Lye Quenched from 1425 Degrees Fahr.

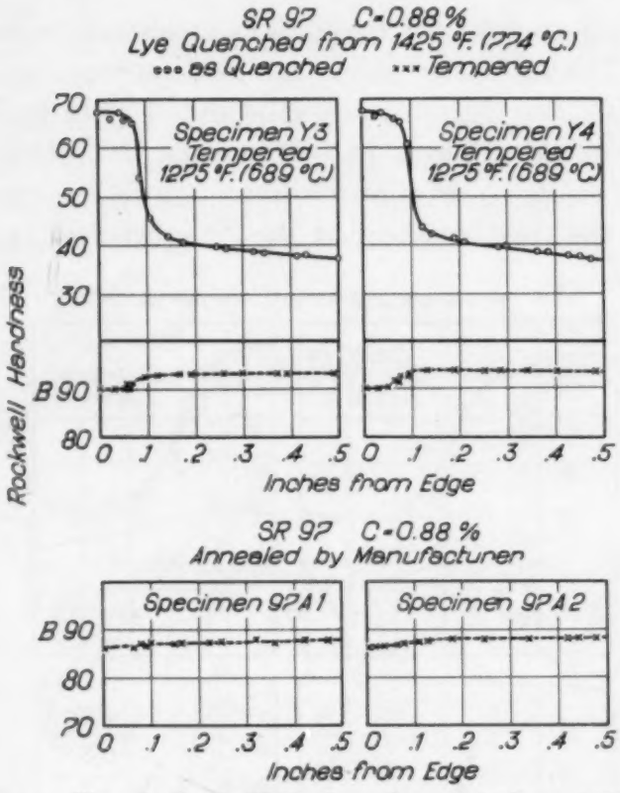


Fig. 5—Steel SR97 Lye Quenched from 1425 Degrees Fahr.

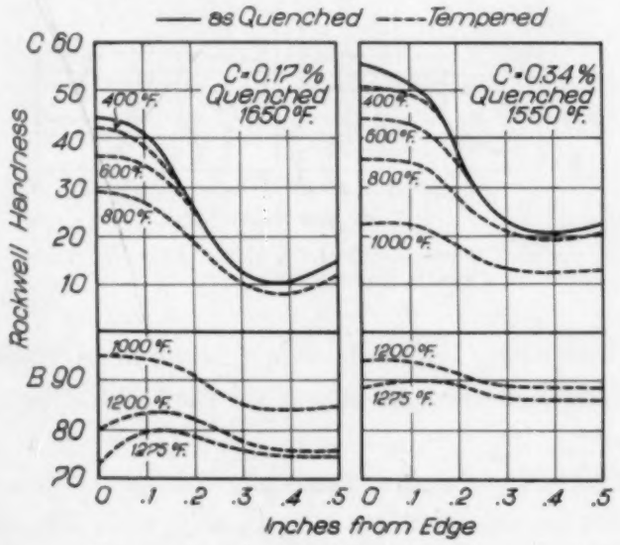


Fig. 6—Averaged Results of the Effect of Tempering on Two Different Steels.

To avoid the possibility of a misunderstanding, it should be pointed out that the traverses for the annealed specimens given in Fig. 5 apply to material that was only given an anneal, without the application of any quenching treatment.

The average results for the various steels are presented in Figs. 6, 7 and 8. The following points are evident from an inspection of the curves: (1) The martensitic shell shows a considerable decline in hardness before any change in hardness is observable in the core. (2) The core starts to drop in hardness before the martensitic shell is lowered to the core hardness of the "as-quenched" material. (3)

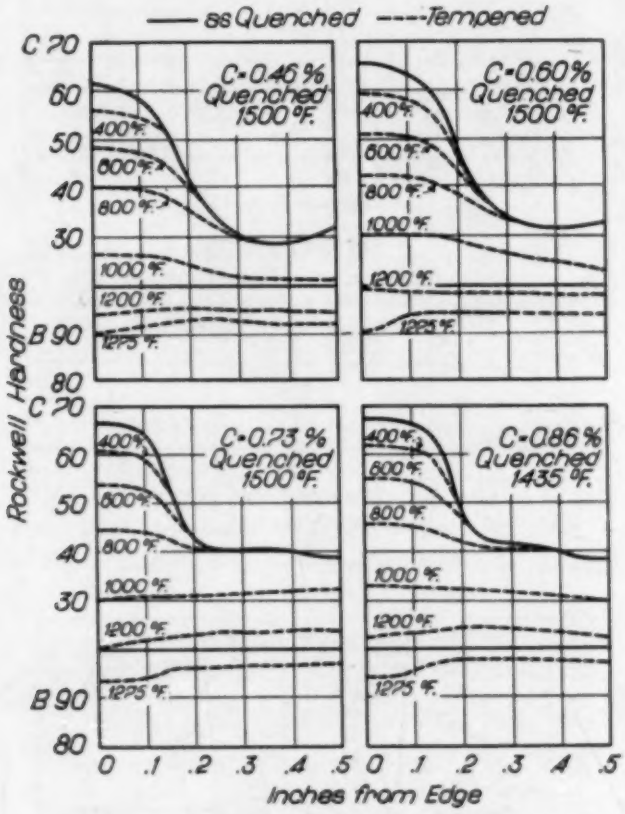


Fig. 7—Averaged Results of the Effect of Tempering on Four Different Steels.

At the higher tempering temperatures, a reversal of relative hardness occurs, with the outer shell of tempered martensite becoming softer than the core.

The reversal of hardness at the higher temperatures indicates that primary troostite is not identical structurally with the decomposition products of martensite. If it were held that primary troostite had the same structure as the decomposition products of martensite it would follow that a series of flat hardness traverse curves would be obtained for those tempering temperatures above that needed to bring shell and core to identical hardness. The experimental curves, however, show that this condition is not fulfilled, hence it must be

concluded that primary and secondary troostite are not structurally identical.

Surface Hardness Versus Carbon Content—In Fig. 9 are plotted curves showing the variation of surface hardness with carbon content. The curve for the "as-quenched" state is in good agreement with similar curves presented by other writers.[3,4]

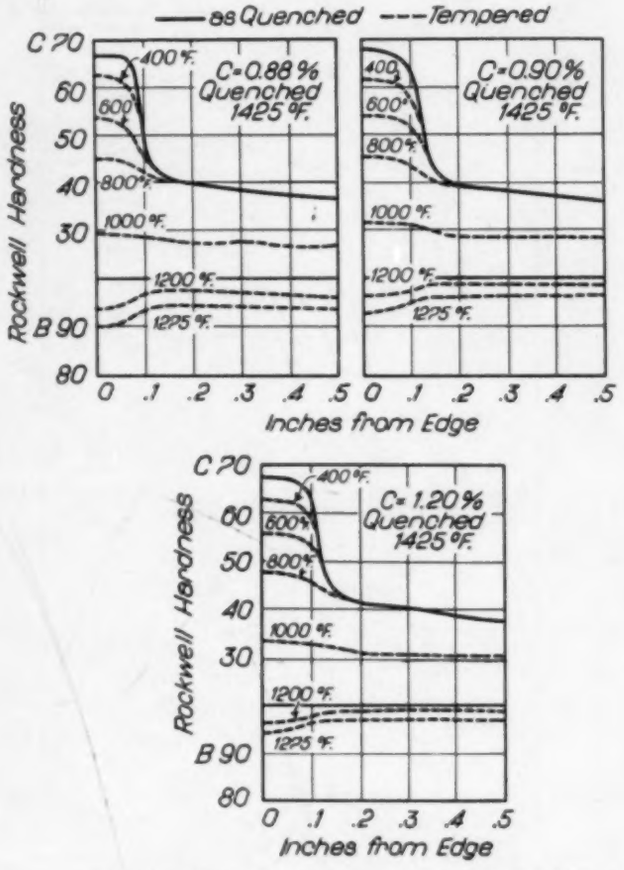


Fig. 8—Averaged Results of the Effect of Tempering on Three Different Steels.

The curves for various tempering temperatures show that the general form of the curve for "as-quenched" material is retained; that is, the curve rises rather rapidly up to approximately 0.7 per cent carbon, beyond which the rate of increase is more gradual. It may be pointed out that as the tempering temperature rises, the difference between the tool steels and the forging steels becomes more apparent.

It should be pointed out that microscopic examination of the

[3]J. L. Burns, T. L. Moore and R. S. Archer, "Quantitative Hardenability," TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 1-36.

[4]H. J. French and O. Z. Klopsch, "Quenching Diagrams for Carbon Steels in Relation to some Quenching Media for Heat Treatment," TRANSACTIONS, American Society for Steel Treating, Vol. 6, 1924, p. 251-294.

various "as-quenched" specimens showed a completely martensitic structure (with free carbide in the case of the three tool steels) at the outer surface, with no primary troostite present. This was true even with the specimens of the lowest carbon content (0.17 per cent).

Macroscopic Examination—The "as-quenched" specimens, after polishing and etching, all had the general appearance shown by the

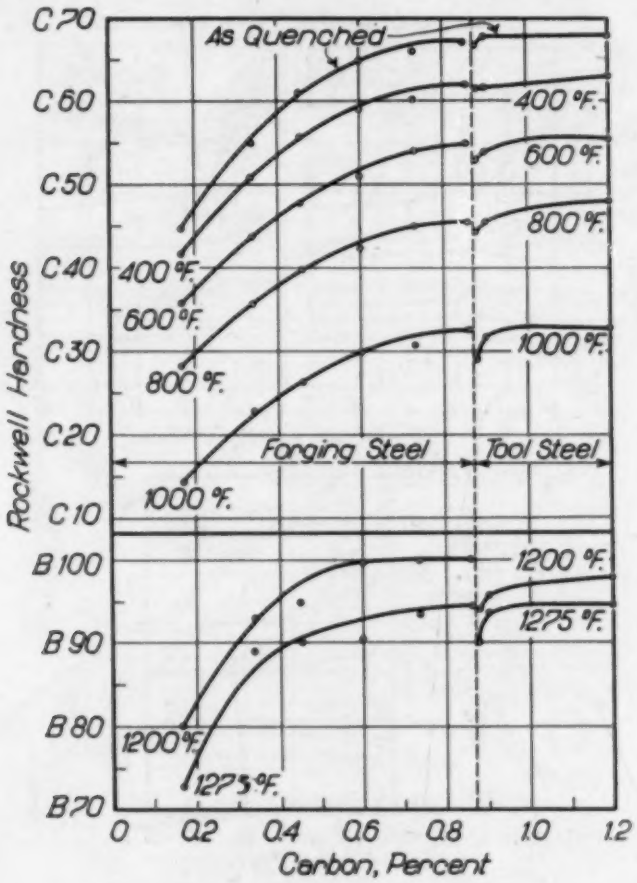


Fig. 9—Showing Variation of Surface Hardness with Carbon Content.

upper specimen of Fig. 2. On tempering, the sharply delineated distinction between shell and core gradually faded, but it is of interest to note that even after tempering at 1275 degrees Fahr. (690 degrees Cent.), the outer shell could still be distinguished from the core. This suggested that differences in microstructure would be observed between shell and core, even at the highest tempering temperatures.

Microscopic Examination—One specimen of each kind was polished and etched for metallographic examination, and studied under high magnification.

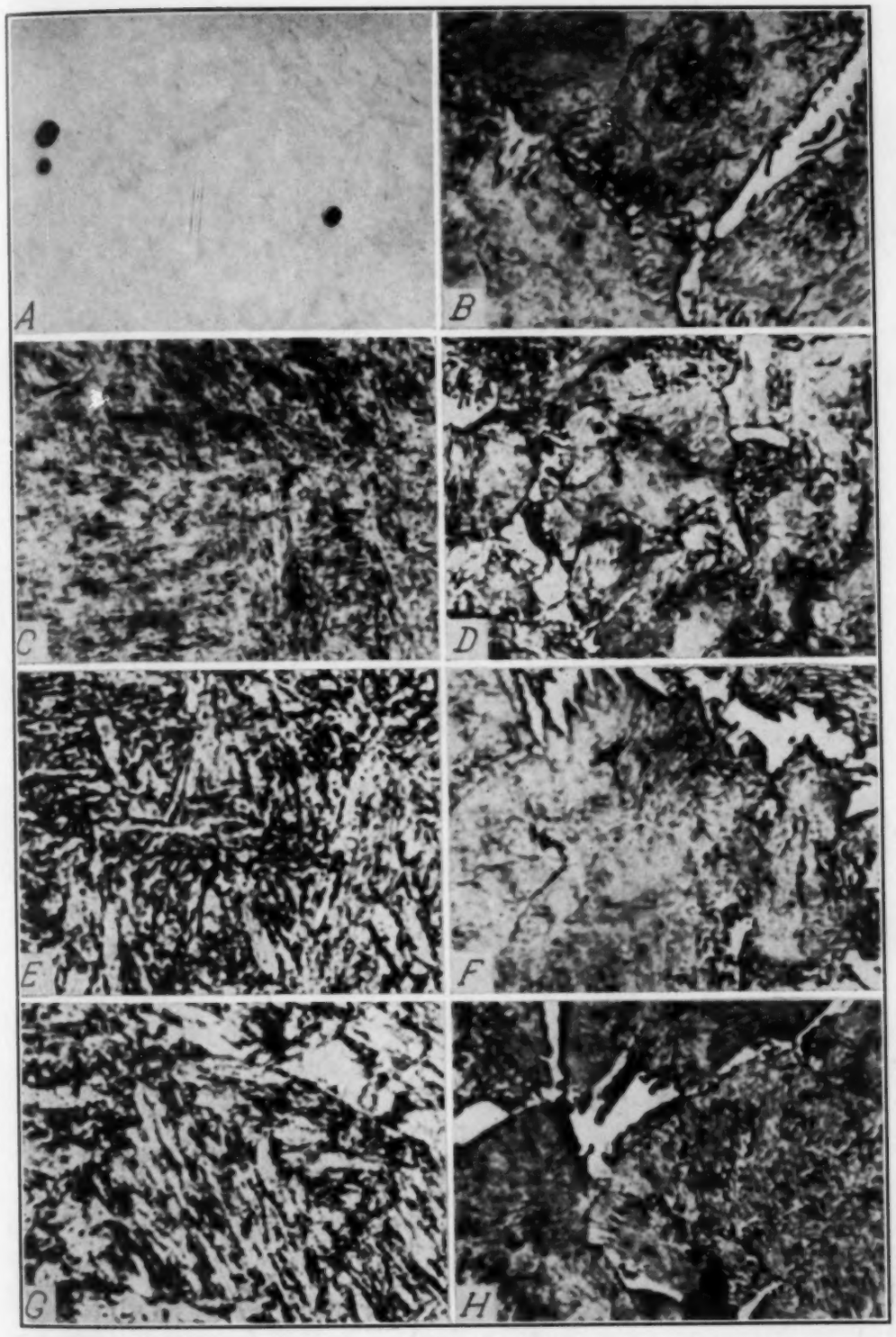


Fig. 10—Photomicrographs Showing Typical Shell and Core Structures of Hypoeutectoid Forging Steel. Carbon Content 0.46 Per Cent; Etchant, 5 Per Cent Picral, 5 Seconds. × 2000.

Shell		Core
A	As-Quenched	B
C	Quenched and Tempered at 400 Degrees Fahr.	D
E	Quenched and Tempered at 600 Degrees Fahr.	F
G	Quenched and Tempered at 800 Degrees Fahr.	H

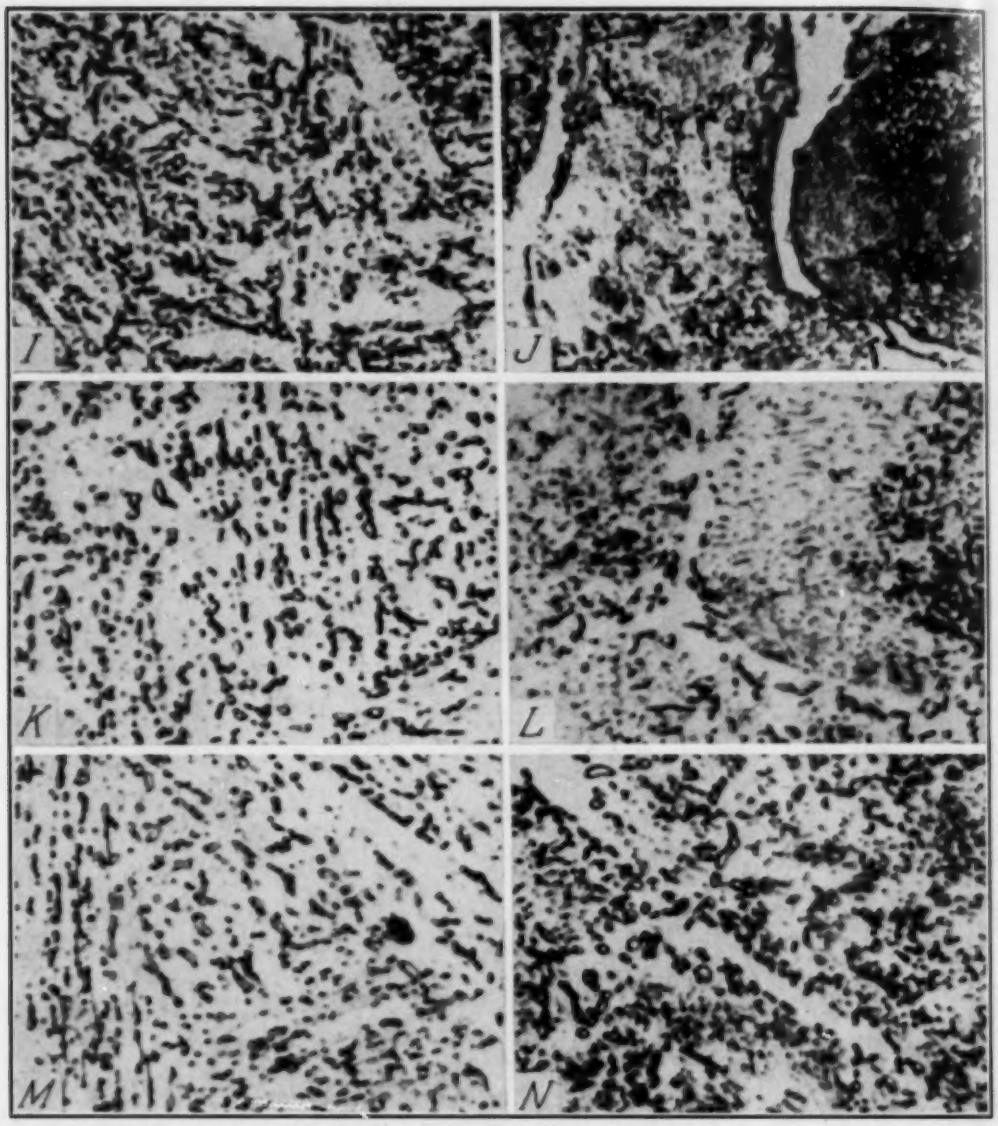


Fig. 10—Photomicrographs Showing Typical Shell and Core Structures of Hypoeutectoid Forging Steel. Carbon Content 0.46 Per Cent; Etchant, 5 Per Cent Picral, 5 Seconds. × 2000.

Shell		Core
I	..... Quenched and Tempered at 1000 Degrees Fahr.	J
K	..... Quenched and Tempered at 1200 Degrees Fahr.	L
M	..... Quenched and Tempered at 1275 Degrees Fahr.	N

Figs. 10, 11 and 12 show typical shell and core structures for a hypoeutectoid forging steel (C = 0.46 per cent), a tool steel of approximately eutectoid composition (C = 0.88 per cent) and a tool steel of hypereutectoid composition (C = 1.20 per cent). In the preparation of these photomicrographs, an etching time of 5 seconds in 5 per cent picral was used for all of the specimens. This etch was insufficient to develop clearly the structure of the martensite in

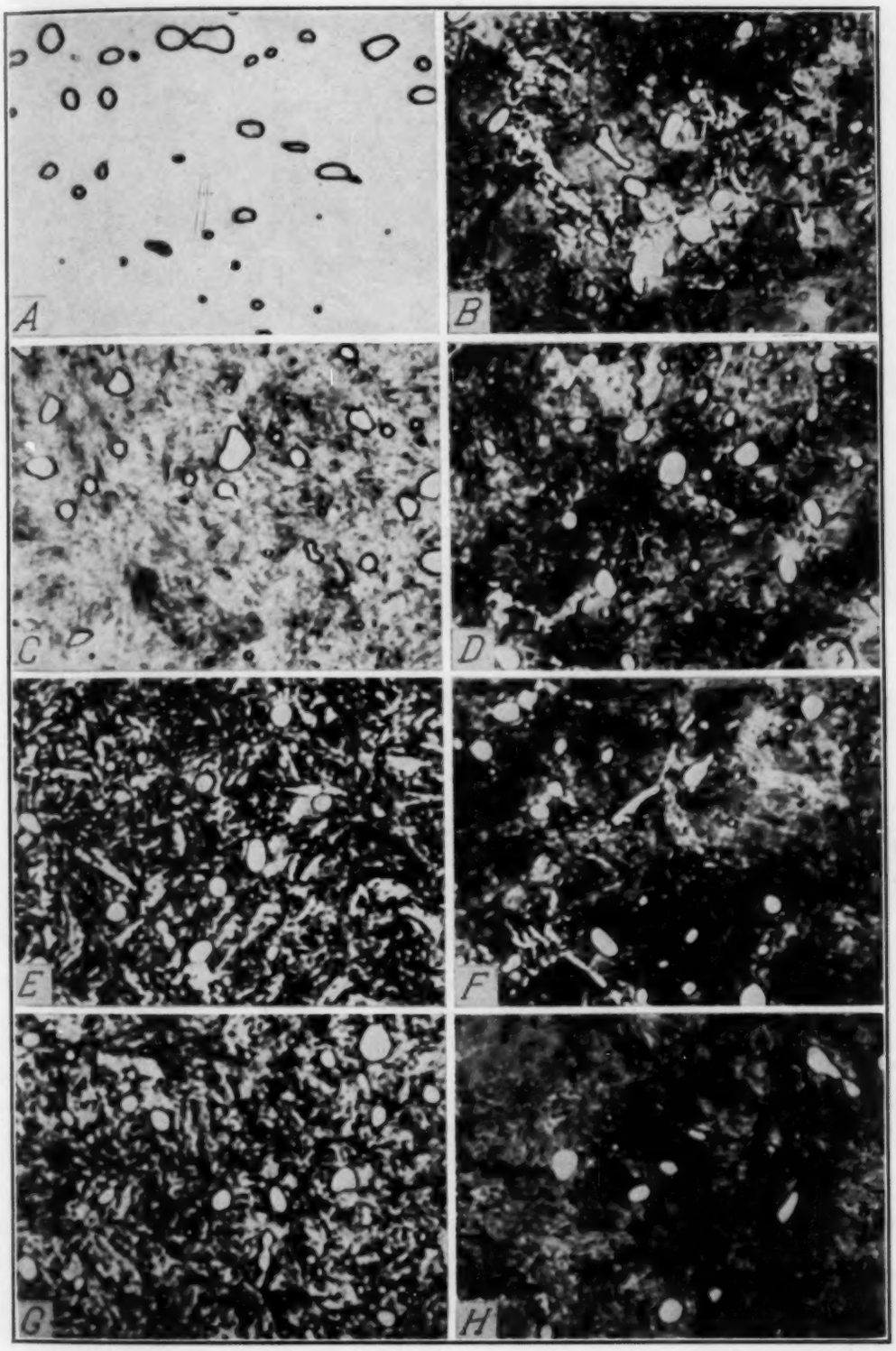


Fig. 11—Photomicrographs Showing Typical Shell and Core Structures of Hypereutectoid Tool Steel. Carbon Content 0.88 Per Cent; Etchant, 5 Per Cent Picral, 5 Seconds. × 2000.

Shell		Core
A	As-Quenched	B
C	Quenched and Tempered at 400 Degrees Fahr.	D
E	Quenched and Tempered at 600 Degrees Fahr.	F
G	Quenched and Tempered at 800 Degrees Fahr.	H

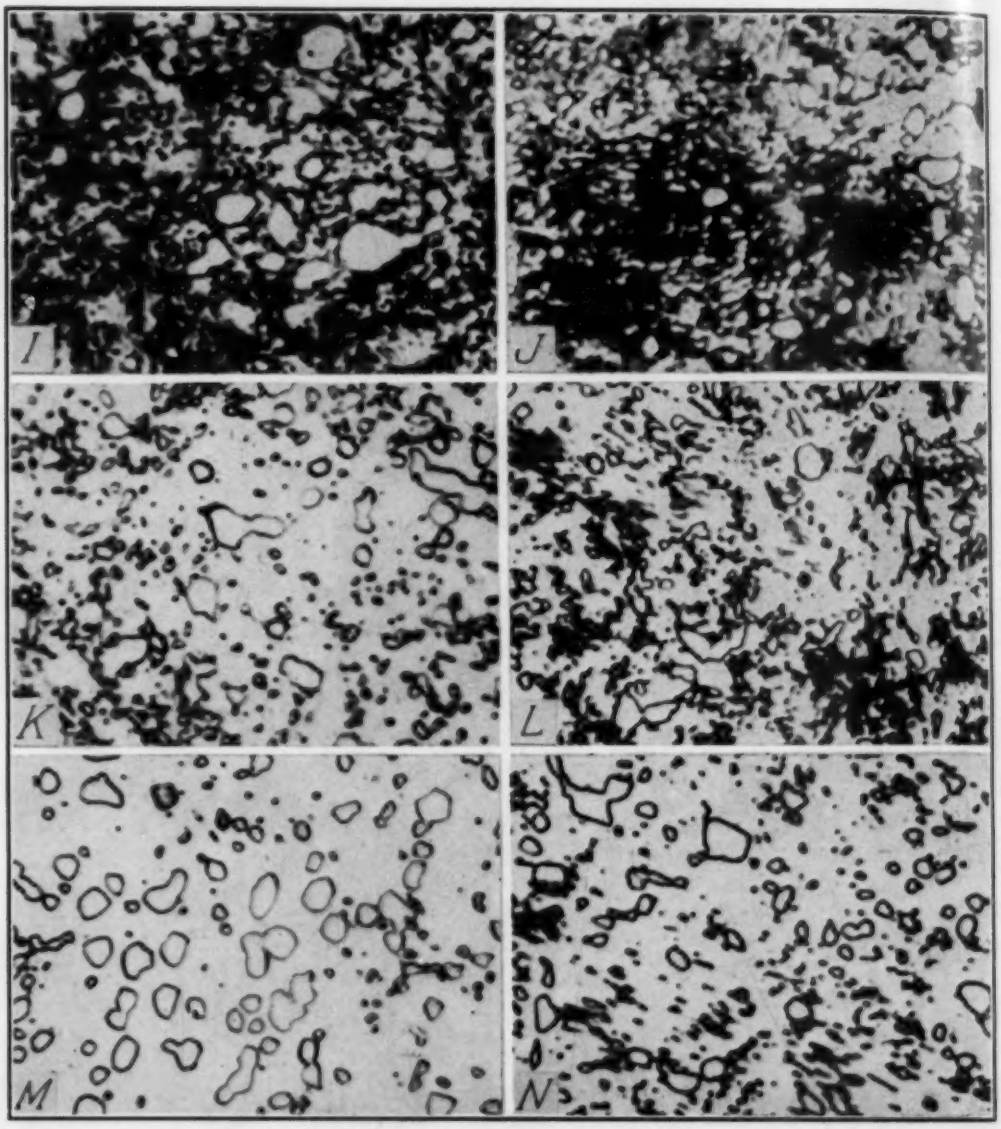


Fig. 11—Photomicrographs Showing Typical Shell and Core Structures of Hypereutectoid Tool Steel. Carbon Content 0.88 Per Cent; Etchant, 5 Per Cent Picral, 5 Seconds. × 2000.

Shell		Core
I	..... Quenched and Tempered at 1000 Degrees Fahr.	J
K	..... Quenched and Tempered at 1200 Degrees Fahr.	L
M	..... Quenched and Tempered at 1275 Degrees Fahr.	N

the "as-quenched" specimens, and perhaps was somewhat too strong for the martensite tempered at 600 and 800 degrees Fahr. (315 and 425 degrees Cent.). However, it was felt that a uniform etching procedure applied to all of the specimens would serve to emphasize more forcibly the changes produced by tempering.

In general, it was observed that the martensitic shell shows detectable changes at tempering temperatures of 400 degrees Fahr.

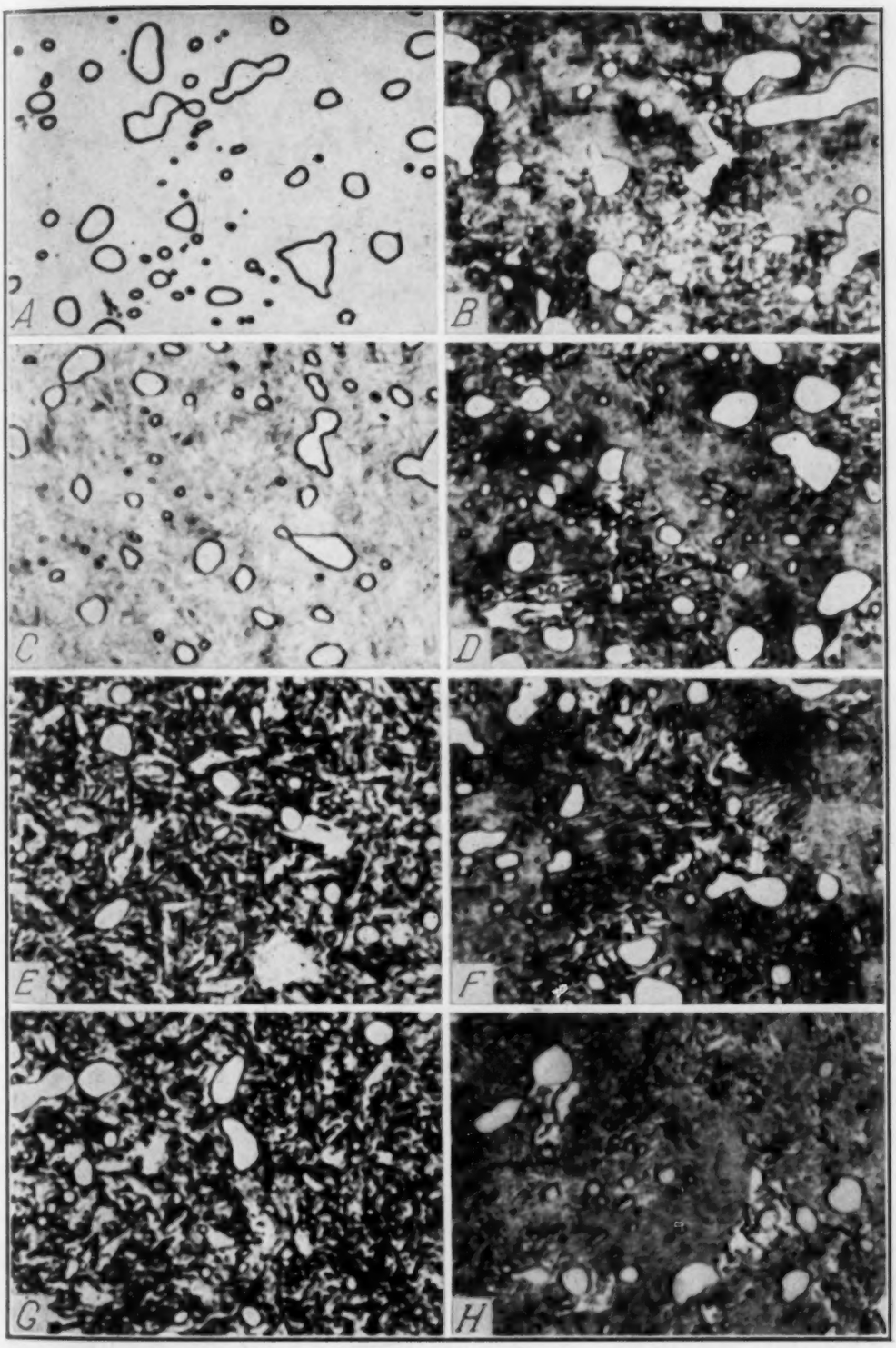


Fig. 12—Photomicrographs Showing Typical Shell and Core Structures of Hypereutectoid Tool Steel. Carbon Content 1.20 Per Cent; Etchant, 5 Per Cent Picral, 5 Seconds. × 2000.

Shell		Core
A	As-Quenched	B
C	Quenched and Tempered at 400 Degrees Fahr.	D
E	Quenched and Tempered at 600 Degrees Fahr.	F
G	Quenched and Tempered at 800 Degrees Fahr.	H

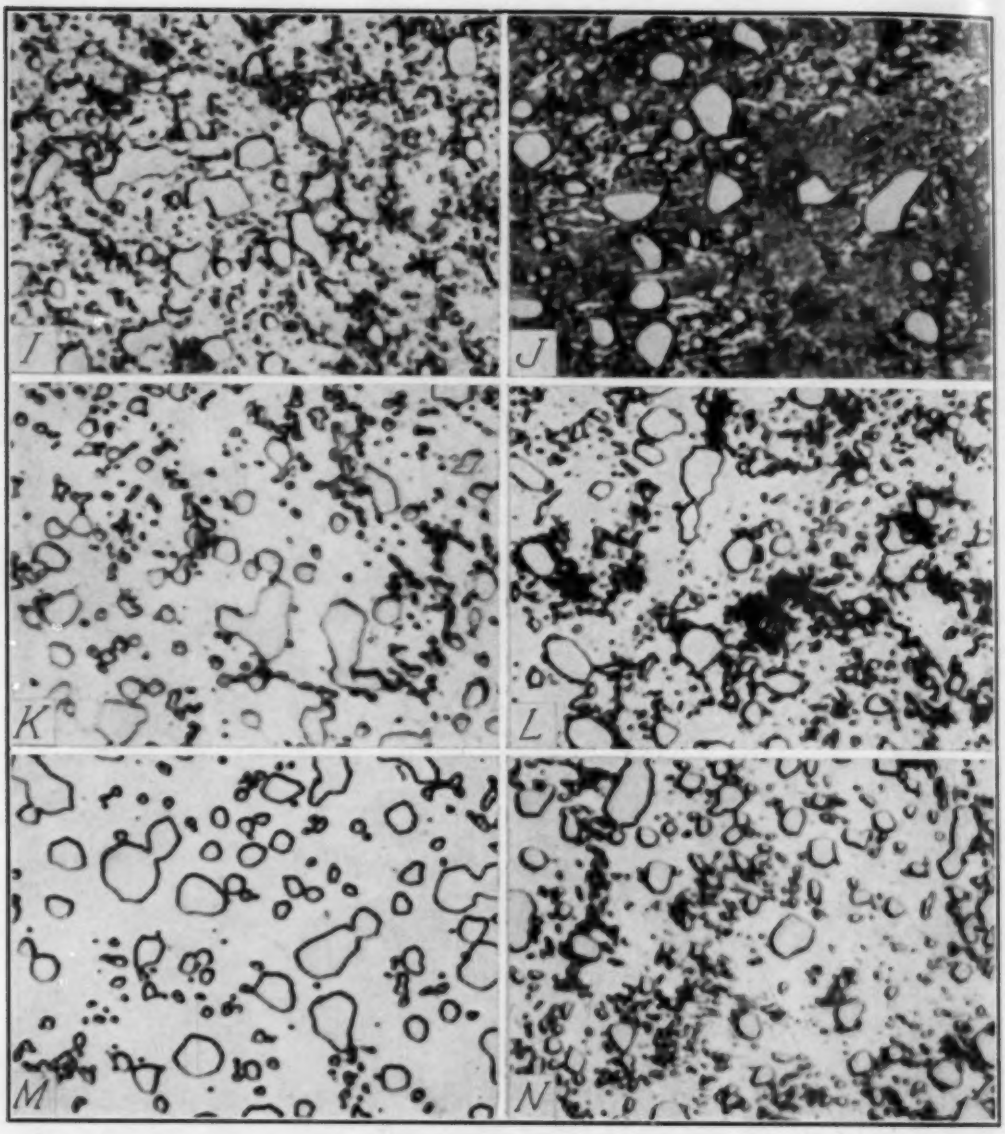


Fig. 12—Photomicrographs Showing Typical Shell and Core Structures of Hypereutectoid Tool Steel. Carbon Content 1.20 Per Cent; Etchant, 5 Per Cent Picral, 5 Seconds. × 2000.

Shell		Core
I	..... Quenched and Tempered at 1000 Degrees Fahr.	J
K	..... Quenched and Tempered at 1200 Degrees Fahr.	L
M	..... Quenched and Tempered at 1275 Degrees Fahr.	N

(205 degrees Cent.) and beyond. The core of fine pearlite shows detectable changes in structure at tempering temperatures of 1000 degrees Fahr. (540 degrees Cent.) and higher. The shell and core exhibit different structures at all tempering temperatures, even at the highest temperature used, 1275 degrees Fahr. (690 degrees Cent.). At the higher tempering temperatures, the shell shows a more coarsely spheroidized structure than does the core, thus explain-

ing the fact that for these tempering temperatures, the shell hardness falls below that of the core.

As the carbon content is lowered below the eutectoid point, there is an increasing tendency for ferrite to make its appearance in the core of the "as-quenched" specimens. In such instances, ferrite is naturally observed in the core of the tempered specimens. Fig. 10.

The forging steels show the same general variations in structure exhibited by the tool steels. However, they are deeper hardening, and some martensite occurs in the central core. The forging steels also exhibit a slower rate of cementite coalescence than the tool steels.

From the foregoing, it is apparent that excellent correlation was obtained between the hardness gradient curves and the structural changes observed in the microscopic study.

Summary and Conclusions

1. Hardness traverses on 1-inch diameter rounds are presented for nine plain carbon steels (0.17 to 1.20 per cent carbon) in the quenched condition, and after tempering at 400, 600, 800, 1000, 1200, and 1275 degrees Fahr. (205, 315, 425, 540, 650, and 690 degrees Cent.).

2. The above curves show that on tempering at progressively higher temperatures:

(a) The martensitic shell shows a considerable decline in hardness before any change in hardness is observable in the core.

(b) The core starts to drop in hardness before the martensitic shell is lowered to the core hardness of "as-quenched" specimens.

(c) The tempered martensitic shell becomes softer than the tempered core at the higher tempering temperatures.

3. The relative hardness changes obtained in tempering the martensitic shell and the central core lend additional support to the view that on tempering martensite, no product is formed which is similar in structure to primary troostite.

4. Microscopic examination reveals distinct differences between outer shell and inner core, even at the highest tempering temperatures.

5. A plot of surface Rockwell hardness versus per cent carbon, both "as-quenched" and after tempering at various temperatures, shows that the hardness rises quite rapidly up to approximately 0.7 per cent carbon, beyond which the rate of increase declines markedly.

ACKNOWLEDGMENT

The writers wish to express thanks to the Wisconsin Alumni Research Foundation for the scholarship grant which made this research possible.

Oral Discussion

R. L. DOWDELL:[1] Martensite and troostite is getting so complicated that many of us really wonder what martensite actually is. I noticed when Mr. Rowe presented his paper he mentioned white martensite. That is really the only martensite that I know as martensite. Do you have black martensite, etc.?

PROFESSOR RAGATZ: I think we intended to imply its appearance after etching and we are not implying that there is more than one martensite.

PROFESSOR DOWDELL: We still agree and as far as this particular group is concerned we take it that martensite is still white?

C. L. SHAPIRO:[2] Although I do not wish to disagree with Professor Dowdell, I wish to say that many investigators have reported that martensite may exist in two forms—the alpha and beta conditions. These structural conditions are observed under the microscope by their etching characteristics. The alpha condition is the normal acicular white martensite observed in quenched steels; whereas, the beta condition is brown martensite and results from tempering slightly white martensite.

PROFESSOR DOWDELL: Then it really is not martensite?

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[1]Professor of Metallography, University of Minnesota, Minneapolis.
[2]Consulting Engineer, Syracuse, N. Y.

SOME OBSERVATIONS ON THE PASSIVITY OF STAINLESS STEELS

By J. N. Ostrofsky

Abstract

Treatment of stainless steel with strong nitric acid as a final processing step has long been practiced in order to remove surface contamination and promote a passive surface condition. Various passivity-activity borderline corrosion conditions were used in this work to study the extent of benefits derived from such treatments. It was found that strong nitric acid acted primarily as a cleaner, but had some value as a passivating agent. Better films were developed by very weak nitric acid used boiling. For some corrosive conditions, particularly where pitting was involved, dichromate solutions gave excellent results.

Dichromates were also added to the weak nitric acid solutions to prevent etching of lower chromium content stainless steels.

Nitric-hydrofluoric acid mixtures appeared to activate stainless steel surfaces, and the activity persisted in part for some time.

STAINLESS steels are rather readily attacked by highly ionized reducing acids, such as hydrochloric acid. They are then said to be in the *active* condition. They ordinarily show little if any attack even after prolonged exposure to oxidizing agents such as nitric acid and are then said to be in the *passive* condition. Early in their history it was observed that if stainless steels were first immersed in certain oxidizing agents, notably nitric acid, and subsequently exposed to solutions which ordinarily attacked them quite readily, no attack occurred or attack was noticeably lessened. This abnormal resistance persisted for some time, occasionally, for years. During this period the steel might be said to be in an *abnormally passive* condition. Monypenny[1] cites many interesting examples. A simple explanation is found in the oxide film theory. Since remarkably protective oxide films are formed spontaneously on exposure to air,

[1]J. H. G. Monypenny, "Stainless Iron & Steel," Second Edition, 1931, p. 260, 314, 347-366. John Wiley & Sons, Inc., New York City.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The author, J. N. Ostrofsky, is chief chemist, Rustless Iron and Steel Corporation, Baltimore, Maryland. Manuscript received June 23, 1938.

it is logical to expect that more impervious films might be formed by certain vigorous chemical agents.

We have been warned to avoid this abnormally passive condition in making corrosion tests, and very properly so, since in many passivity-activity[2] borderline corrosion conditions slight changes in extent of passivation will often completely alter behavior. Nevertheless having once established the fitness of a certain stainless alloy for a given service, there is good reason for taking advantage of any additional protection afforded by simple chemical treatments. This insures an optimum film condition during at least the initial period of service.

Passivation, it is true, cannot be relied upon to permanently prevent attack under conditions in which the alloys are normally active. On the other hand, damage can occur in the early stages of some types of service because a covering of dirt or grease received in fabrication has greatly restricted the formation of sound surface films. Passivation could very well eliminate this difficulty and would give added assurance against damage to fine equipment.

For years the most widely used passivation treatment for stainless steels has consisted of washing or immersing in strong nitric acid, usually 20 to 40 per cent acid, used warm for periods up to 1 hour or more. This treatment serves two main purposes:

1. *Cleaning.* Nitric acid of the strength used readily attacks surface contamination, such as particles of iron, copper or pickling smut, and "brings up" the white silvery color of clean stainless steel.

2. *Passivating.* The strongly oxidizing properties of the acid effect replenishment and repair of weaknesses in the more or less impervious oxide films which characterize stainless steels.

There is probably no better agent available for performing this first function—cleaning—than 20 to 40 per cent nitric acid. This follows because of all materials commonly encountered in processing, stainless steels alone are undissolved by acid of this strength. Whenever a vigorous cleaning treatment is required, strong nitric acid either alone, or, if some slight etching can be tolerated, mixed with a small amount of hydrofluoric acid, will be found effective and economical.

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[2]For a more complete discussion of the passivity-activity boundary concept the reader is referred to R. J. McKay and R. Worthington, "Corrosion Resistance of Metals and Alloys," 1936, p. 286. Reinhold Publishing Corp., New York City.

For the second function—bolstering of the oxide film on a clean surface—other agents are available which appear to be much more effective than strong nitric acid. Very weak nitric acid, for instance, containing only $\frac{1}{10}$ to 1 per cent acid by weight, used boiling, will develop films which are demonstrably superior and more often impenetrable in passivity-activity borderline corrosion conditions than those produced by strong acid. When used on clean surfaces, boiling alkali dichromates—about 5 per cent solutions—are excellent passivating agents, particularly against pitting or where drop staining is involved.

These strong film builders are not particularly effective as cleaners, since their action on iron, organic matter and the like is much less vigorous than that of stronger acid. They will not remove pickling smut readily, and the preferred method of passivating after pickling would include first, cleaning in strong nitric acid, and finally passivation with the weaker solutions. Perhaps the drastic oxidizing action which characterizes a good cleanser for stainless steel, produces too coarse an oxide film for best corrosion resistance.

Weak nitric acid is practically a hydrogen liberating acid to 12 per cent chromium alloys, and etches these alloys very rapidly at the boiling point. Little effective passivation could be expected under these conditions. The addition of ½ per cent potassium dichromate serves to completely inhibit etching, and excellent passivation results. For example, a solution of ½ per cent HNO_3-½ per cent $K_2Cr_2O_7$, used boiling for 30 minutes, will not cloud or color a micro polish on a 0.35 per cent carbon, 13 per cent chromium steel in the plain hot-rolled condition.

The following laboratory data will illustrate the passivity effects discussed above. Much of the work described is admittedly of a qualitative nature. Since corrosion conditions are complex, the author would certainly urge actual operating tests before any departures from standard treatments are made. Possibilities in the surface treatment of alloys which develop such remarkable films are intriguing and the data is presented more in an attempt to point out possibilities in one phase of surface preparation than in an attempt to prescribe definite treatments. In most cases the *breakdown* of complete passivity was chosen as an index of the effectiveness of the passivating treatment; having established this breakdown from inspection of specimens, of the solution and, in doubtful cases, from weight loss measurement, no attempt was made to measure corrosion rates in the semi-active period immediately following breakdown. It

was felt that normal rates would be retarded during this period and could very well be erratic and confusing.

Series A—Samples of a straight chromium steel (0.10 per cent carbon, 15.56 per cent chromium) were cut from a deep drawn kitchen utensil and exposed with rather rough edges and without relieving residual or shearing stresses to pickling and passivating. They were then exposed in a reflux condenser to boiling 4 per cent acetic acid containing 1 per cent sodium chloride. This is a passivity-activity borderline condition for stainless steel of the above composition. In this test the duration of passivity is readily measured, since a generous evolution of hydrogen indicates the end of the passivity period.

The various treatments used and the results obtained are described in Table I. Although the utensil without passivation was immediately attacked by the boiling solution, prior passivation with weak acid resulted in complete absence of attack during one week's exposure. Passivating with strong acid showed some improvement over no treatment, but passivity failed early. With this particular utensil both pickling and cleaning prior to passivation were necessary for best results. The use of nitric-hydrofluoric solutions combined pickling and cleaning, and specimens so pickled were readily passivated by the weak acids. HNO_3-HF appeared to have little or no value as a passivating agent. On the contrary, it appeared to produce an active surface condition—an observation substantiated by experiments on the adhesion of copper and zinc films described later.

Series B—Tests with a boiling mixture of 3 parts sulphuric acid, 1 part nitric acid diluted to a total acidity of ½ per cent figured as H_2SO_4, gave interesting results. This test is also a passivity-activity borderline condition for most stainless steels. The test is usually run in a reflux condenser for four 2-hour periods, fresh acid being used each period.

Specimens were saw cut from annealed and pickled 1-inch diameter bars (0.10 per cent carbon, 17.10 per cent chromium) and were only superficially finished with 120 grit aloxite. There was little opportunity for contamination of the specimens in their preparation and no preliminary cleaning or pickling treatments were used before passivation. A fairly large number of tests established the following conclusions:

1. Untreated specimens generally became passive either during the first exposure period or directly thereafter, but always suffered some attack before becoming passive.

2. Specimens treated for a short time in previously used solution, i.e., containing ferric and chromic sulphates, as well as residual nitric acid and sulphuric acid, were always found to be completely passive at once to fresh solution.
3. Specimens treated for various lengths of time with the usual passivating agents, i.e., 30 per cent to concentrated nitric acid at room temperature or warmed, were seldom better than untreated specimens.
4. Specimens boiled in 0.1 to 0.5 per cent nitric acid *exhibited passivity at once* and remained passive.
5. Alkaline oxidizing agents, such as solutions of sodium peroxide, or alkaline ammonium persulphate increased activity to the solution.
6. Boiling in 5 per cent potassium dichromate or chromic acid was not effective in producing passivity.

In these tests untreated specimens usually showed an induction period of one or two minutes duration before attack took place. Treatments with agents mentioned in No. 5 noticeably reduced this period. The termination of passivity is readily noted in these tests by a sudden evolution of hydrogen and an abrupt change in the color of the specimens.

Series C—On the other hand—and somewhat contradictory—in tests of annealed bar stock in the 4 per cent salt spray, treatments with boiling ½ per cent to 5 per cent potassium dichromate gave excellent results. The development of water-breaks in the condensed spray on these specimens was considerably delayed as compared with specimens not so treated. Evidently, the type of oxide film produced by dichromates is particularly effective in resisting droplet corrosion. Portevin[3] has recently called attention to "wetting ability" of greaseless surfaces as an index to their activity. Boiling treatments with $\frac{1}{10}$ to 1 per cent HNO_3 were not quite so effective but were good. Treatment with stronger nitric acid for various lengths of time seemed to show an increasing pit size with increasing acid concentration. Perhaps action on nonmetallics or difficulty in rinsing strong acids from nonmetallic pores is an explanation of this observation.

Series D—Work which was done in an attempt to copper-plate stainless steels by immersion is of interest in connection with the activation of stainless steel surfaces. A 5 per cent cupric chloride

[3]A. Portevin, Paris letter, METAL PROGRESS, Vol. 34, No. 1, July, 1938, p. 62.

Table I

Exp.	Pickling Treatment[1]	Cleaning Treatment[2]	Passivating Treatment[3]	Behavior in Boiling 4% Acetic Acid—1% NaCl	Remarks
1	None	None	None	Attacked at once.	Utensil is normally active to the test condition.
2	H_2SO_4	HNO_3(A)	None	Passive 1 hour, then attacked.	Customary pickling and passivating treatment produced temporary immunity.
3	H_2SO_4	HNO_3(B)	Weak acid	Passive, removed after 48 hours.	Customary pickling and passivating treatment, coupled with weak acid treatment, produced immunity to test conditions.
4	H_2SO_4	HNO_3(B)	None	Passive ½ hour, then attacked.	Omission of weak acid treatment resulted in early breakdown of passivity.
5	H_2SO_4	None	Weak acid	Passive 1 hour, then attacked.	Failure to thoroughly clean specimens before passivation resulted in early loss of passivity.
6	H_2SO_4 (20 min.)	None	Weak acid	Passive, removed after 4 hours.	Extended pickling appeared to produce more easily passivated surface. However, repeated in Exp. No. 11, below, passivity failed early.
7	None	None	Weak acid	Passive 1 hour, then attacked.	On this utensil, pickling, cleaning and weak acid treatments were needed to produce passivity.
8	HNO_3-HF	No other	None	Attacked at once.	HNO_3-HF appears to activate the surface.
9	HNO_3-HF	No other	Weak acid	Passive, removed after 6 hours.	HNO_3-HF combines pickling and cleaning.
10	Same as Exp. No. 3, above, but large sample partially immersed in reflux.			Passive, removed after 1 week.	Compare with Exp. No. 4.
11	Same as Exp. No. 6, above, but large sample partially immersed in reflux.			Passive at first, attacked during first night.	Bears out need for cleaning.

[1]Either 10 per cent H_2SO_4, 5 minutes at 120 degrees Fahr. or 10 per cent HNO_3-½ per cent HF, 5 minutes at 130 degrees Fahr. All percentages by weight.
[2]A. 10 per cent HNO_3, 30 minutes at 120 degrees Fahr.
B. 25 per cent HNO_3, 5 minutes at 120 degrees Fahr.
[3]½ per cent HNO_3, 30 minutes boiling.

solution containing about 9 per cent hydrochloric acid by weight will produce, by simple immersion, a rather good copper-plate on the iron-chromium stainless steels, even those containing as high as 27 per cent chromium. Adhesion of the plate will be very poor, however, unless the article to be plated is first activated by several minutes immersion in nitric-hydrofluoric acid solution. This activation persists in part for an appreciable time—at least several days. Poor adhesion followed treatment with muriatic acid, although fairly good results were obtained with chemically pure hydrochloric acid.

Corollary experiments were made with electro-zinc plating. Samples of 15-16 per cent chromium wire were given preliminary dips of two to five minutes at room temperature in the following solutions, all expressed by volume:

25 per cent muriatic acid
25 per cent hydrochloric acid
10 per cent nitric acid, ½ per cent hydrofluoric acid
10 per cent nitric acid

The samples were then plated in three types of zinc solution with the results shown below. Adhesion was measured by 180-degree flat bend tests on ⅛-inch wire. If no flaking occurred, the results were considered good.

	Adherence of Plate After Treatment In			
Solution	Muriatic Acid	HCl	HNO_3-HF	HNO_3
Zinc Chloride, 2 minutes	Poor	Poor	Good	Good
Zinc Sulphate, 2 minutes	Poor	Poor	Good	Poor
Zinc Cyanide, 30 minutes	Good	Good	Good	Poor

Here again nitric-hydrofluoric solution stands out as an effective activator and cleanser.

Series E—A ½-inch diameter x 4½ inch 17 per cent chromium bolt was passivated with boiling ½ per cent nitric acid for one-half hour and exposed to 25 per cent by weight sulphuric acid, the threaded end being partially immersed. After five years' exposure this specimen is still completely unattacked.

A bolt passivated simply by normal exposure to air was completely converted to salts in this solution in a very few days. If simple chemical treatments give such substantial protection against very active solutions, the protection they should afford in more normal service must be very considerable, especially so if the films produced are not so fragile or delicate that the least disturbance disrupts them.

Some discussion of their strength seems called for. Most of the samples used in this work were purposely chosen with rather rough finishes which would be expected to be quite sensitive to damage. Passive samples could be handled quite roughly, even sometimes scratched lightly, and still remained passive in very active solutions. The films are not quite so fragile as one might first believe. Sheet can be bent moderately without necessary damage. Screws, for instance, in several pound batches can be passivated in a basket, and after considerable handling incidental to rinsing, transferring and packaging will be found to have retained their passivity to normally active solutions.

In conclusion, it should be emphasized that there was no thought in any of this work of inducing a purely artificial passivity on stainless steel and using it in this condition against normally active solutions, as for instance, 10 per cent sulphuric acid. The work was done principally in connection with individual problems as they arose, and was carried along because of its general interest. There are, of course, many cases where an easily handled and effective passivation can be of considerable use. An example is the prevention of light rusting, during storage, on packaged parts such as valves, hub caps, screws, kitchen-ware and the like. In the chemical field, thorough passivation at certain intervals could often be practiced at no great expense, and would be helpful in extending the life of costly equipment, particularly where the service involved is near borderline.

No attempt has been made in preparing this paper to review existing patents relative to its subject matter or to indicate that one or another of the several procedures discussed may be covered by patents.

In closing the author wishes to express his appreciation to his associates, especially to W. B. Arness, for helpful advice and criticism throughout the work. To the management of the Rustless Iron and Steel Corporation thanks are due for their friendly interest in fostering the work.

DISCUSSION

Written Discussion: By Dr. B. Egeberg, chief metallurgist, International Silver Co., Meriden, Conn.

The author has combined a number of experiments, all dealing with activation and passivation treatments of straight chromium stainless steels, into a paper which essentially is a plea for recognition of the value of surface treatments. The subject dealt with by Mr. Ostrofsky is of great importance to many of us. Electroplaters are interested in methods for complete activation since electrodeposits will not adhere properly to stainless steels unless the protective film is entirely removed. (Certain industries practice the plating on stainless steel). On the other hand, artificially increased passivity is of interest in many fields, especially where service conditions are such as to make one expect a somewhat lasting benefit, and further, where hardenability is a factor, thus preventing one from utilizing the highest corrosion resistant steels of the chromium-nickel type.

Dealing first with the electroplaters' needs, an effective film removing treatment, void of etching or dulling of a highly polished surface, was first developed in the writer's laboratory some five years ago. In principle it con-

sists of a cathodic treatment in a strongly activating bath containing hydrochloric acid and nickel chloride, the solution being so adjusted that the cathode efficiency of the nickel is extremely low. Hydrochloric acid, nascent hydrogen and dissolved chlorine all contribute towards an effective removal of film. In time the steel will be covered with an exceedingly thin and completely adherent deposit of nickel which makes it possible to transfer the article through rinse tanks and through air to the final electroplating bath without passivation of the surface taking place. Without this protective film of nickel, stainless steel would be partly passivated by the oxygen content of the rinse waters, not to speak of the transfer through air from tank to tank, whereby intimate contact and complete adherence of deposit to base would be prevented.

Speaking now of those cases where a mechanically strong film of low permeability is desired for the purpose of added corrosion protection, the first question that arises is how to test the properties of the films and to discriminate between them after they have been applied artificially by certain selected treatments. Mr. Ostrofsky has solved the problem by using liquids of considerable corrosive strength and by noting the duration of passivity. The corrosive media were so selected that termination of passivity was signified by a definite endpoint, namely gas evolution or color change of specimen.

While the method seems excellent for the purpose, the writer would like to mention a variation which Mr. Ostrofsky may want to try since in a shorter time it affords the possibility of finer discrimination between films of nearly equal protective value. It was used by the writer some years ago with considerable success. Also in this case a testing medium of some activity is used; for example, a copper sulphate solution acidified with sulphuric acid. The single potential of the stainless steel in this solution was measured against a calomel half-cell with a potentiometer. It was found that a properly hardened and freshly polished stainless steel sample (0.35 per cent carbon, 13.5 per cent chromium) showed a single potential immediately after immersion of about 0.6 volt which would soon rise to higher values. If the potential at the beginning was less than 0.6 volt (steel improperly hardened) copper started to deposit and the readings rapidly dropped to the value corresponding to the single potential of copper in the solution mentioned. If the properly hardened steel were exposed to the atmosphere for considerable periods of time before subjected to test, the initial reading was higher than 0.6 volt and might reach a value as high as 0.8 volt, rising to 1 volt on a sample tested one year after being polished and stored in the meantime under normal atmospheric conditions in a closed box. The conclusions of the investigation were that polished stainless steel, when exposed to the atmosphere, rapidly improved its protective film for the first few days to one week after which time further improvement was slow. The polish referred to is the so-called mirror finish obtained commercially with cotton buffs and abrasive grease cakes. This operation causes considerable heating of the article which in itself should promote protective film formation. The method should be applicable also to artificially produced films such as those dealt with by Mr. Ostrofsky. The initial potential (immediately after immersing the sample in the test solution) is evidently the significant figure. To allow time for making this reading, test solutions must be used which do not too rapidly alter the surface condition.

Besides the testing method used, I have also cited the results in order to justify a bit of criticism on Mr. Ostrofsky's paper. He states on page 744 that activation of the surface takes place by immersion in a mixture of nitric and hydrofluoric acid and that this activation persists in part for at least several days. This is in good agreement with my own findings as cited above, only I would extend the same statement to film removers in general, including mechanical abrasion. After having read Mr. Ostrofsky's paper several times, it is not clear to me if this vital point has been taken sufficiently into consideration: that stainless steel requires considerable time for developing passivity of its own accord and under normal atmospheric conditions, whereas an artificial passivation, such as used by Mr. Ostrofsky, is rapidly accomplished. It seems that he has made a comparison between samples passivated by various solution agents on the one side and, on the other, samples which have been activated during their preparation and which, due to an insufficient rest period, may still have been in a partly active condition when subjected to test.

While such samples may have some interest, the reader is unable to locate reference to samples which have been properly treated in normal atmosphere for a proper length of time, say for at least two days and, preferably, for one week. Mr. Ostrofsky has controlled details as to time and temperature of the artificially passivated samples and similar details concerning natural passivation in the atmosphere are equally as important in order to draw a comparison between the two.

Written Discussion: By Dr. U. R. Evans, Cambridge University, Cambridge, England.

The practical importance of Mr. Ostrofsky's main observation—that dilute nitric acid is superior to concentrated nitric acid in preparing the surface of stainless steel to withstand "borderline conditions"—will be obvious to all readers. To me it has also considerable scientific interest, as the observation fits in well with certain facts lately noticed by myself in connection with the passivity of ordinary (chromium-free) iron and steel[4] towards natural waters.

It has been found impossible to make ordinary iron or steel passive for any length of time merely by soaking the abraded surface in chromate solution. This is probably because the shattered zone left by abrasion is very difficult to passivate, owing to its unstable structure and the internal stresses which keep cracking any film produced on it. If the shattered zone was removed by etching, then it was found that the rugged, crystalline surface left behind could be rendered passive more easily; the iron could subsequently be kept in natural waters for some time before rusting sets in. In the case of steel, a further improvement was brought about by using, instead of pure potassium chromate, a mixture of chloride and chromate in proportions adjusted so as to eat away any specially susceptible spots and then leave the remainder passive. On pure iron, where there are no "chemically different" spots, chloride-free chromate gave almost as good results as the mixture.

It is always a little risky to try to interpret the results of another investigator, but tentatively I would apply the same principles to explain the interesting results obtained by Mr. Ostrofsky. Concentrated nitric acid, a strong oxidizing agent, will produce more effective resistance to attack than dilute

[4]U. R. Evans, *Nature*, 1938, Vol. 142, p. 160.

nitric acid *so long as the steel is in the nitric acid.* But for that very reason, the susceptible spots present in the steel are left undestroyed by the concentrated acid, and when the steel is *subsequently* exposed to borderline conditions, the passivity readily breaks down. In the boiling dilute acid, the susceptible spots are eaten away, and the etched surface left behind is easier to protect; on cooling down the acid, a reliable film is formed on this surface, especially if dichromate is present, and the metal, which has lost its special susceptible particles, withstands borderline conditions comparatively well.

As regards the action of hydrofluoric acid, fluorine ions have been found to have a penetrating power for films, similar to, although inferior to that possessed by chlorine ions.[5]

Passivity is due to protective films, but the power of a given film to withstand breakdown, whether by a passage of an anion inwards or a cation outwards, is related to the magnitude of the energy change which would accompany the passage of the ion in question. Thus the chance that a given film may confer protection will depend on the stability of the structure of the metal below it, and particularly on freedom from residual, tensile stress, a state which always favors film-breakdown.[6]

The idea that a mirror-finish is the condition most likely to confer safety from corrosion may require a little reconsideration. A surface bounded by a perfect crystal-face, such as is obtained by etching, is a stable surface, and usually constitutes a safe basis for a protective film. Even the absence of a single atom from the surface will enormously reduce the work of removing the atoms which adjoin the "hole," a matter which can be investigated mathematically, but which is qualitatively well known to anyone who has tried to unpack a box of child's bricks. The surface layer on metal which has been polished mechanically represents a disorganized mass, which is specially susceptible to certain reagents—as was indeed shown in the classical work of Sir George Beilby. It may sometimes be better to remove this layer before covering the remaining mass of metal with the protective film. It is on these lines that the present attempts at Cambridge to make ordinary (chromium-free) iron and steel passive against natural waters are proceeding. None of the results as yet obtained are of any practical importance, but they are encouraging since they show that the principle is sound; it is hoped that the work, which is now being taken over by Dr. Agar, will progress rapidly.

Written Discussion: By H. A. Smith, metallurgist, Republic Steel Corp., Massillon, Ohio.

First we would like to say that we are heartily in accord with the author's discussion pertaining to the practical application of passivating treatments for stainless steels. It is not sound to depend upon artificially passivated finishes under conditions where the steel would not render satisfactory service if not passivated. Nor should steel for such applications be passivated before testing where the test is at all designed to simulate service conditions.

In the author's work, which has all been on the straight chromium type of steel, it is found that HNO_3-HF pickling or cleaning agents render such steels

[5]S. C. Britton and U. R. Evans, *Chemistry and Industry,* Vol. 49, No. 14, 1930, p. 173T.

[6]U. R. Evans, *Journal Chemical Society,* 1939, p. 97.

active. We agree that on the chromium steels this is the case. However, in our experience with the austenitic chromium-nickel types of stainless, we find that a 10 per cent HNO_3-½ per cent HF pickle does not render the surface particularly active. In activity such a treated surface is between a good HNO_3 passivation and a HCl-H_2SO_4 pickle.

As the author points out, grease on the surface of the stainless steel may give rise to failure in certain applications. We have found this to be true even when the grease exists on top of the passivated finish. To be more specific—grease and foreign matter should be removed as thoroughly as possible before any passivation treatment, so that such treatment can be as uniform as possible. Moreover, for most satisfactory service—the steel should be kept as free from foreign matter as practicable.

The statement that alkaline or neutral oxidizing agents are not as effective as acidic oxidizing agents for passivating of stainless steels gives me an opportunity to express some ideas, which have been developing for some time. If the passive film on stainless steels partakes of an oxide nature, it is probably of an acidic nature, as chromium oxides are usually acidic in their reactions. Thus, under very strongly basic conditions such passive films should be broken down. This we know to be actually the case. Therefore, alkaline or neutral oxidizing agents, while tending to form a passive film because of their oxidizing nature, also tend to break it down because of their alkaline reaction. The usually superior behavior of molybdenum-bearing 18-8 under acid conditions may be explained on the same basis, inasmuch as molybdenum oxides are even more acidic in their reactions than the oxides of chromium.

There is one point about which my ideas are not too clear. Mr. Ostrofsky states that the preferred method of passivating after pickling would be a cleaning in a strong nitric acid solution followed by passivating in a weak solution of the same acid. It is also stated that strong acid treatments are not as good as weak acid treatments for passivating. Can this be interpreted to mean that the weak acid passivation in some way strengthens the weak places in the film formed by the strong HNO_3 cleaning, so that the results are those to be expected by a weak acid treatment used singly upon a surface cleaned by, say, some mechanical means? I am wondering about the efficacy of a double nitric acid treatment.

Author's Reply

I want to thank Dr. Egeberg for his very interesting discussion, and am glad that he has introduced the subject of passivation through aging in air. There is no question in my mind that this is one of the most important factors in the preservation of stainless steel surfaces. Variations in surface potential, as wide as those shown by him to occur in the course of one or two weeks aging, would undoubtedly affect the results obtained in any borderline corrosion test. This is a point that those of us engaged in accelerated test work on stainless steels would do well to consider. His criticism of the present paper in this regard is well taken.

Surface condition during aging is, of course, also important. Grease or dirt will restrict passivation by chemicals or by air alone, and one requirement for a standardized aging period should be that the surfaces are chemically

clean and are kept so during aging. Dr. Egeberg's method of activation prior to plating sounds like a very satisfactory one. A quite different and adverse effect is obtained if any metals are present which can plate out by simple replacement. This condition does occur—more frequently in muriatic acid than in sulphuric acid solutions—when a plating rack carrying copper on contact areas is repeatedly passed through an activating bath.

The author appreciates Dr. Evans' comments. His many publications on the oxide film theory have been invaluable in working with the stainless alloys. It has been our experience also that best passivation is obtained when slight etching accompanies the treatment. Frequently, however, etching is undesirable from an appearance standpoint, and most of the work described in the present paper has been directed towards passivation treatments which did not manifestly alter the surface appearance. Some selective attack very likely does occur with boiling dilute nitric acid, as Dr. Evans suggests, but there is little evidence of it microscopically. Fink and Kenny have described[7] an anodic passivation for stainless steels which results in marked etching but produces remarkably uniform point-to-point potentials.

The author agrees with Mr. Smith that a requirement for good passivation is that grease and foreign matter be removed either in the treatment or before it. Frequently, immersing in strong nitric acid is sufficient, but there are many cases that require special treatment. The method of continuous potential measurement with a recording potentiometer described[8] by Mr. Smith should be very useful in studies of this kind.

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[7]C. G. Fink and F. J. Kenny, "The Passivity Produced by Chromic Acid on 18-8 Chromium-Nickel Alloys," *Transactions*, American Electrochemical Society, Vol. 60, 1931, p. 235.

[8]H. A. Smith, "Pit Corrosion of Stainless Steel," METAL PROGRESS, Vol. 33, June 1938, p. 600.

THE EFFECT OF CARBON CONTENT ON THE RATE OF OXIDATION OF STEEL IN AIR AT HIGH TEMPERATURES

By C. A. Siebert

Abstract

This paper deals with the effect of carbon content on the oxidation of steel in the temperature range 1700 to 2100 degrees Fahr. It has been found that all of the carbon steels showed regions where the amount of scaling decreased with increasing temperature, while Armco iron showed a continuous increase in the amount of scaling with increasing temperature. The difference in behavior of Armco iron and the carbon steels is attributed to decarburization and its effect on the chemical analysis of the scales formed.

THE literature on the subject of oxidation has been reviewed in previous publications from this laboratory by Murphy, Wood and Jominy (1)[1], Upthegrove and Murphy (2), and Siebert and Upthegrove (3); no review will therefore be given at this time. The method used was essentially the same as that reported by Siebert and Upthegrove (3).

The samples used in this investigation were cylinders 5/8 inch in diameter and 2.5 inches long which had been polished with various grades of emery through 000 paper. The furnace used was an electric furnace of the Globar-type which contained a glazed porcelain tube 40 inches long and approximately 2 inches in diameter. One end of the tube was sealed with a two-holed refractory stopper through which the thermocouple protection tube and air inlet tube were led. The sample was introduced into the furnace, through which a stream of dried and purified air was passing, the total time in the furnace being one hour. The drying and purification of the air was accomplished by passing it through towers of calcium chloride, ascarite, and dehydrite. The composition of the steels used is given in Table I.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The author, C. A. Siebert, is assistant professor in the Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Michigan. Manuscript received July 25, 1938.

Table I

Composition of Steels Investigated

	X	Y	A	E
	Per Cent			
Carbon	0.15	0.18	0.47	0.90
Manganese	0.50	0.62	0.65	0.66
Silicon	0.23	0.23	0.19	0.18
Sulphur	0.032	0.023	0.028	0.033
Phosphorus	0.025	0.015	0.18	0.20
McQuaid-Ehn Grain Size	4–5	7	....	....

The analysis for the Armco iron was not obtained.

Results

The scope of this investigation was limited to the effect of carbon content on the oxidation of steel. The data which were obtained when the temperature of exposure was varied from 1700 to 2100 degrees Fahr. (900 to 1150 degrees Cent.) are summarized in Fig. 1. The curves for the steels all show regions where the amount of scaling is actually lowered with increasing temperature. This is in accordance with the work of Upthegrove and Murphy (2), and Siebert and Upthegrove (3), (4). However, the Armco iron curve does not show a region where the amount of scaling is lowered with increasing temperature. As pointed out in previous publications, this decrease in scaling with increasing temperature is due to a difference in the degree of oxidation of the scale itself. As the temperature at which maximum scaling occurs is exceeded, an increasing proportion of ferric iron in the scale is observed. This increase in the ferric iron content changes the character of the membrane through which the diffusion of the oxygen, in some form, must take place. It also changes the solubility of oxygen in the scale, as FeO has a wider solubility range than Fe_3O_4 which alters the driving force (concentration gradient) in the diffusional process. A definite relationship (3) is observed between ferrous iron content of the scale and the loss in weight.

The X and Y steels are both of the S.A.E. 1020 type with different McQuaid-Ehn grain sizes. The X and Y steels both reached a maximum scaling loss at 1900 degrees Fahr. and a minimum at 2050 degrees Fahr. However, the Y steel scaled to a greater extent than the X steel from 1700 to 1950 degrees Fahr., and the X steel to a greater extent than the Y steel from 1950 to 2100 degrees Fahr.

This was shown in a previous publication (4) to be due to differences in grain size at these temperatures.

The A steel is of the S.A.E. 1045 type. The scaling curve for this steel shows a maximum scaling loss at approximately 1875 degrees Fahr. and a minimum at approximately 2025 degrees Fahr. From 1700 to 1900 degrees Fahr. the A steel scales to a greater extent than the X steel, but to a lesser extent than the Y steel. From

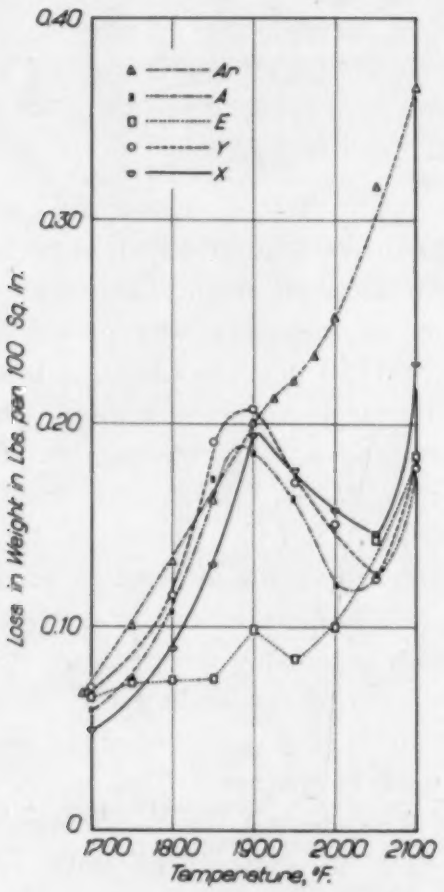


Fig. 1—Curves Showing Amount of Scaling of Steels Tested at the Various Temperatures.

1900 to 2050 degrees Fahr., both the X and Y steels scale to a greater extent than the A steel. At 2050 and 2100 degrees Fahr., the A and Y steels have approximately the same scaling values, while the X steel scales to a greater extent than the A and Y steels.

The E steel is of the S.A.E. 1090 type. The scaling curve for this steel shows a maximum scaling loss at 1900 degrees Fahr. and a minimum at 1950 degrees Fahr.

The oxidation curve for the Armco iron does not undergo a

maximum or minimum change, but continues to increase with increasing temperature. This behavior of the Armco iron accounts for the fact that several investigators, who employed Armco iron, were unable to check our findings of maximum and minimum points in the scaling curves for steel. At 1850 and 1900 degrees Fahr. the A and Y steel scale to a greater extent than the Armco iron, but at all other temperatures investigated, the Armco iron showed the highest scaling loss. The ferrous iron content of the scale formed at several temperatures is given in Table II. These analyses, along

Table II
Ferrous Content of Scale Formed at Different Temperatures

Temperature Degrees Fahr.	Steel				
	AR	A	E	X	Y
1800	....	51.4	29.5	44.1	50.7
1950	47.7	33.3	12.0	41.1	....
2000	41.9	....	....	....	....

with the scaling values shown in Fig. 1, again demonstrate that a high scaling loss is accompanied by a high ferrous iron content in the scale.

Discussion of Results

The data presented in Fig. 1 indicate:

(1) The occurrence of maximum and minimum points in the scaling curve are due to the presence of carbon in iron, and

(2) The magnitude of the scaling loss at any given temperature is not solely a function of the carbon content of the steel.

It is a known fact that the scaling of steel involves not only the oxidation of the iron but also the oxidation of the carbon and other elements in the steel. Assuming that only carbon and iron are involved in the scaling of steel, one pound of oxygen would remove the following:

0.75 pounds of carbon if oxidation product were CO
0.38 pounds of carbon if oxidation product were CO_2
3.5 pounds of iron if oxidation product were FeO
2.6 pounds of iron if oxidation product were Fe_3O_4
2.3 pounds of iron if oxidation product were Fe_2O_3

It is evident from the above calculation that if the rate of diffusion of oxygen through the scale at any given temperature were the same regardless of the carbon content of the steel, then the magnitude of scaling at any given temperature should decrease

with increasing carbon content. However, this is not the case, indicating that the character of the scale formed at any given temperature is influenced by the carbon content of the steel and therefore alters the rate of diffusion. This difference in the scale membranes is also shown by the analysis given in Table II.

The grain size of the steel has been shown (4) to be one of the factors which may alter the character of the membrane. This may account for the fact that from 1700 to 1875 degrees Fahr. the A steel (S.A.E. 1045) scaled to a greater extent than the X steel (S.A.E. 1020) and less than the Y steel (S.A.E. 1020), since the Y steel was fine-grained and the X steel coarse-grained in this temperature range while the A steel showed a mixed grain with a predominance of fine grain.

The presence of maximum and minimum points in the scaling curve are evident in steels shown in Fig. 1, but are absent in the curve for Armco iron. This behavior indicates that carbon is responsible for the reversal in the scaling curves for steel. The elimination of carbon during the oxidation of steel occurs as CO or CO_2, probably a combination of both compounds existing. Since the scale membrane is a continuous layer, the oxide of carbon must dissolve in the scale and diffuse outward from the scale-metal interface. Pfeil has shown (5) that the oxidation of iron is a double diffusional process; oxygen diffusing inward and iron outward through the scale membrane. The oxygen diffusing inward tends to oxidize the scale to a higher degree of oxidation, that is, FeO to Fe_3O_4 and Fe_2O_3, while the diffusion of iron outward tends to counteract the diffusion of oxygen inward, keeping the scale in a lower degree of oxidation. The curve of ferrous iron content of the scale versus temperature has been shown (2), (3) to follow very closely the shape of the loss in weight versus temperature curve. The scale formed on Armco iron at 2000 degrees Fahr. contains 41.9 per cent ferrous iron while the scale formed on an S.A.E. 1020 steel (3) at this temperature would contain 15 to 20 per cent ferrous iron. Therefore, the diffusion of the oxide of carbon outward through the scale membrane, when steel is undergoing oxidation, must decrease the diffusion of iron outward, thereby allowing the scale to reach a higher degree of oxidation. It is possible that the oxide of carbon dissolving in the scale may materially decrease the solubility of iron in the scale, which would decrease the rate of diffusion of iron outward through the scale.

No explanation can be offered at the present time as to why decarburization should become so active at temperatures above 1850 degrees Fahr. However, the above explanation appears to satisfy the observed experimental data.

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1. D. W. Murphy, W. P. Wood and W. E. Jominy, "Scaling of Steel at Elevated Temperatures by Reaction with Gases and the Properties of the Resulting Oxides," TRANSACTIONS, American Society for Metals, 1932, Vol. 19, p. 193.
2. C. Upthegrove and D. W. Murphy, "Scaling of Steel at Heat Treating Temperatures," TRANSACTIONS, American Society for Metals, 1933, Vol. 21, p. 73.
3. C. A. Siebert and C. Upthegrove, "Oxidation of a Low Carbon Steel in the Temperature Range of 1650 to 2100 Degrees Fahrenheit," TRANSACTIONS, American Society for Metals, 1935, Vol. 23, p. 187.
4. C. A. Siebert and C. Upthegrove, "The Effect of Grain Size on the Oxidation of Low Carbon Steel," Preprint No. 12, 1937, American Society for Metals.
5. L. B. Pfeil, "The Oxidation of Iron and Steel at High Temperatures," *Journal*, Iron and Steel Institute, 1929, Vol. 119, p. 501.

AUTOMATIC POLISHING OF METALLURGICAL SPECIMENS USING CAST IRON AND LEAD LAPS

By Tracy C. Jarrett

Abstract

This paper describes a method of polishing metallurgical specimens by the use of cast iron and lead laps.

Flatness, freedom from flow of metal and the retaining of inclusions are highly important factors in polishing.

The use of the method described herein tends to accomplish these objectives, and results from this method are given in the paper.

PREPARING metals for microscopic investigation has been the topic of considerable discussion. Several articles have been published dealing with this subject and it is the object of this paper to further this knowledge by describing a different method.

The polishing of metallurgical specimens for microscopic examination by the use of paper and cloth laps has been thoroughly described by F. F. Lucas[1] and J. R. Vilella.[2] This type of polishing is the one most widely used today and precision results have been obtained. If great care is taken, specimens can be polished this way without bringing about a flow of metal. There is a natural tendency, however, when a piece of metal is polished with a cloth lap for the metal to flow, and this may obliterate the structure under examination. This is more pronounced in the case of soft metals, and when inclusions are the subject of examination they will often be torn loose from their parent metals.

In the method about to be described, it appears from the results obtained that this tendency of the metal to flow and inclusions to be pulled out, are lessened. This may be explained by the fact that there is a continuous grinding operation through all stages of grinding and polishing, so that in the end a "ground-polished" surface is

[1]F. F. Lucas, "The Preparation of Iron and Steel Specimens for Microscopic Investigation," Transactions, American Society for Metals, Vol. 24, 1936.

[2]J. R. Vilella, "Metallographic Technique for Steel," American Society of Metals, 1938.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. The author, Tracy C. Jarrett is assistant metallurgist, American Optical Co., Southbridge, Mass. Manuscript received June 6, 1938.

the result. There is, however, one thing that should be brought out at this time: it is impossible to rid a specimen from all of its scratches. This, to some, may be a bad feature, but regardless of the few scratches remaining it is possible to see the structure under examination very clearly.

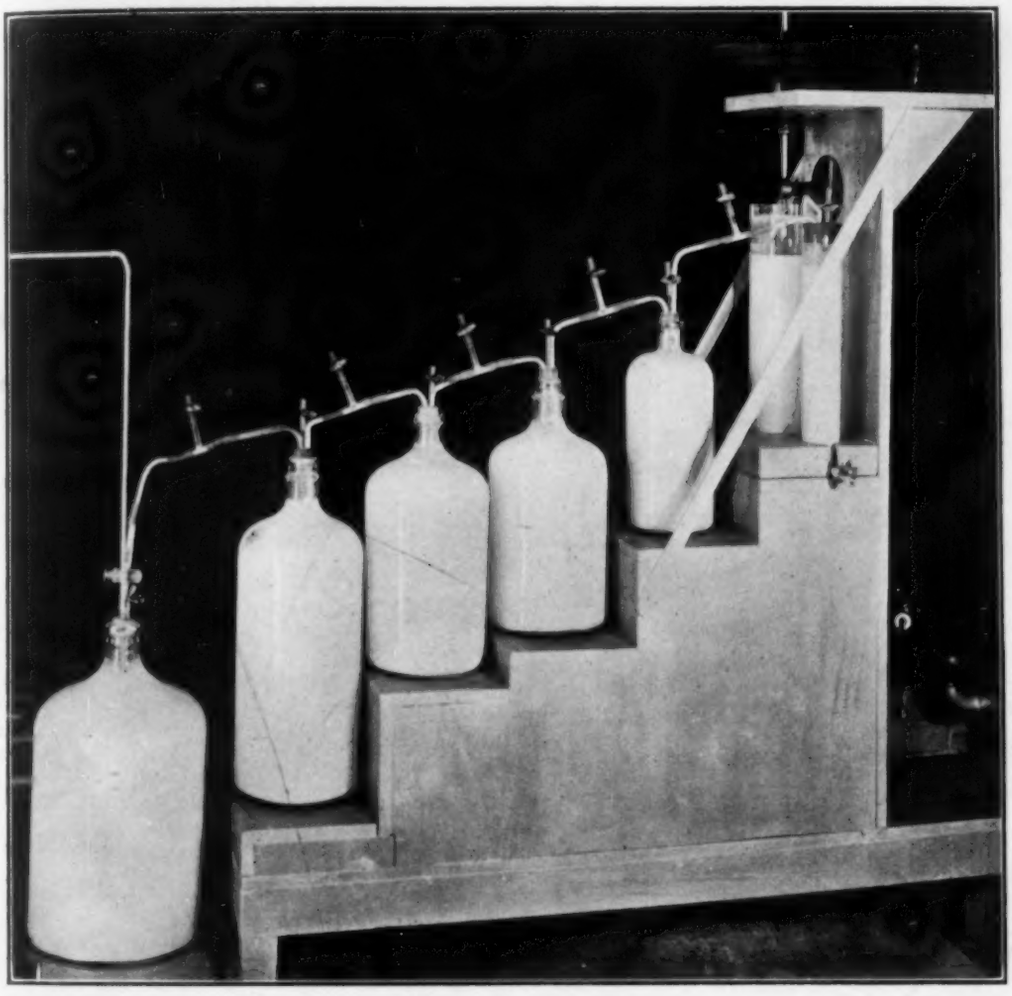


Fig. 1—Levigating Train.

In this method, like that of the cloth laps, there is used a slightly different procedure for soft metals than for hard, the harder metals being much easier to polish than the soft ones.

The first step to consider is the abrasives used, with particular reference to the types of materials and their fineness. For the grinding, the corundum type gives satisfactory results, and for the polishing operations levigated alumina is necessary. The commercial levigated alumina on the market today is not fine enough for this type of

polishing and it is necessary to levigate again. This is done in the following manner: The commercial levigated alumina is ball-milled for a period of about two weeks and then passed through a water levigating train. See Fig. 1. This train is simple and is designed so that a constant rate of flow and a definite speed of stirring are maintained. At certain intervals a predetermined amount of ball mill solution is added. This type of grading gives a very uniform

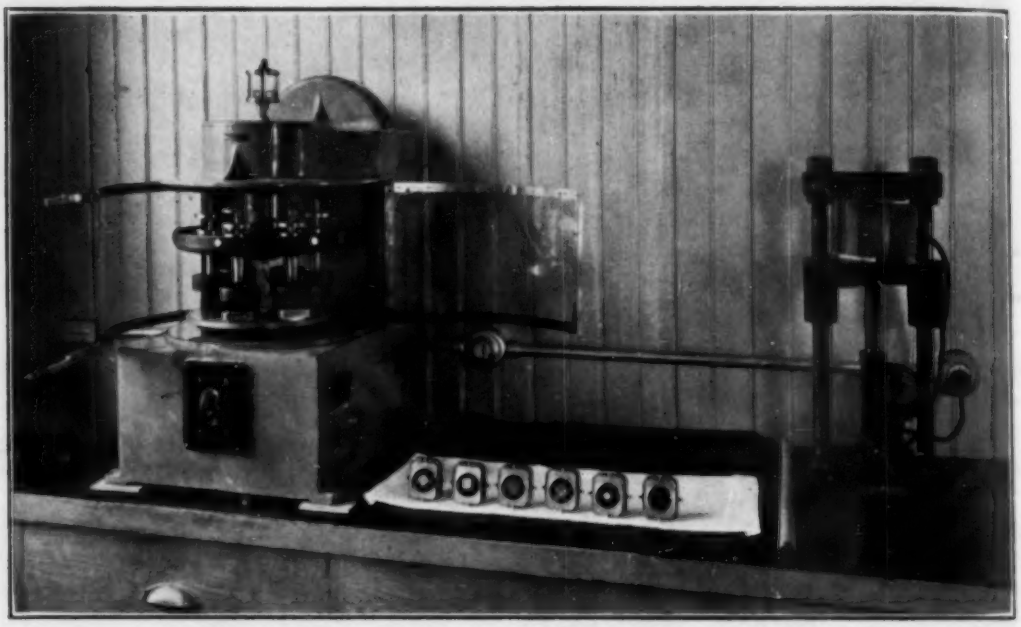


Fig. 2—Automatic Polishing Machine.

particle size, and each successive grade is finer so that when used successive degrees of finer polishing may be obtained. The powder, after levigating, is dried to remove all traces of water and then re-ground in a mortar.

In the grinding and polishing of the specimens, there are three factors that play an important part in the finished work. The first one to consider is the lubrication of the laps. There are on the market today petroleum and vegetable oils that may be used, but they must be free from sulphur and acids. These elements, when present, will cause some specimens to tarnish. The body of the oil must be taken into consideration, as a too heavy oil keeps the specimens away from the lap and retards the speed of grinding and polishing. There is also a tendency in the case of heavy oils for the specimens to drag over the lap and burn the surface. It was found that pure kerosene desulphurized with mercury is the best lubricant to use for the

grinding and polishing. While grinding with a kerosene mixture of M303 to M305 corundum the specimens cut rapidly, and when they are polished with a mixture of kerosene and levigated alumina a bright finish is produced.

The speed of the machine must be such that the lubricant will remain on the lap, but fast enough to produce a high polish and yet not heat the specimens or the lap. When the lap is running too fast



Fig. 3—Photograph of a Polished Specimen of Cast Iron with Monochromatic Light. × 5.

it throws the specimens to the outside with a slight tendency to tip the specimen and produce a high centered surface. The speeds that have given the best results are about 90 revolutions per minute for the lap and about 200 revolutions per minute for the head. The lap in this type of machine runs counter clockwise and the head runs clockwise. See Fig. 2.

The mounting medium used to mount the specimens is also important, as a thermo-plastic material has a tendency to flow during the cycle of polishing. From our own results we have found that the regular Bakelite is the best all-round mounting material to use.

When the above factors are taken into consideration, the polishing technique about to be described may be followed as a general procedure. However, this procedure depends more or less on the specimens to be polished, and the experience of the operator. The polishing time for six specimens by an experienced operator may vary from 2 to 6 hours, depending very much on the specimens being polished.

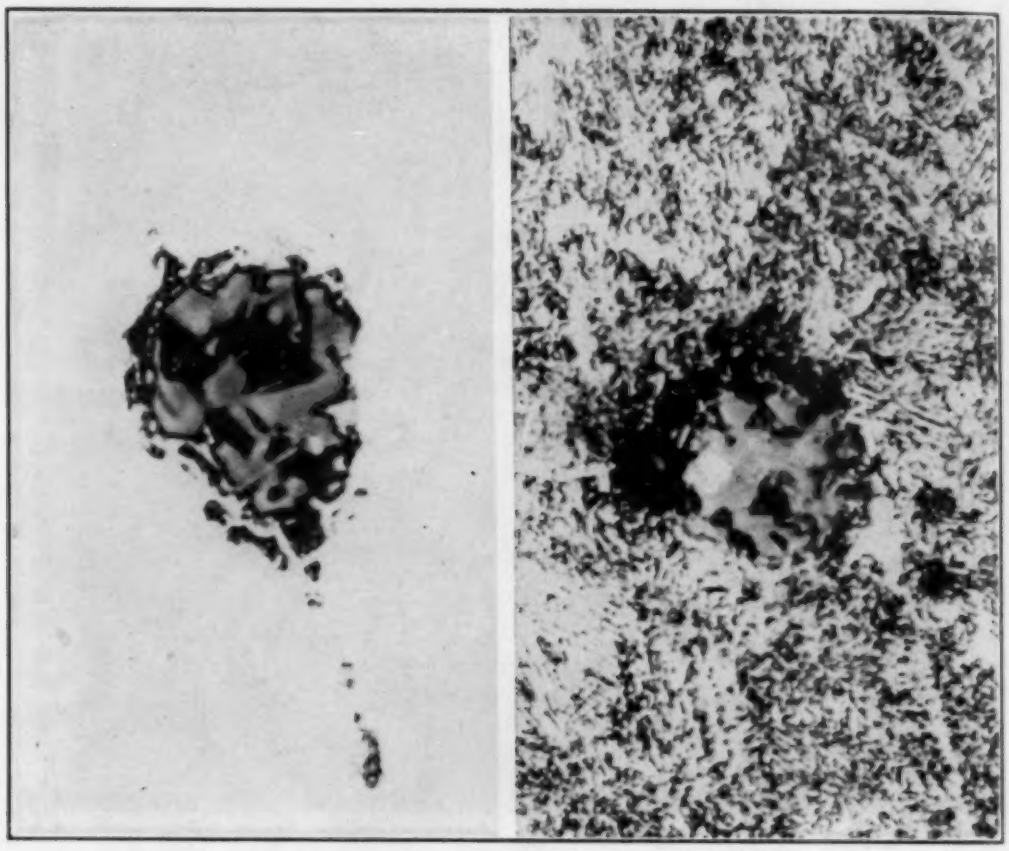


Fig. 4—Photomicrograph of an Inclusion in Manganese Steel. Unetched. × 1000.
Fig. 5—Photomicrograph of Inclusions in Manganese Steel. Etched in Nital. × 1000.

Steel specimens polish easier and faster than brass or gold. In general, it may be said that ease and speed of polishing become more difficult the softer the specimens.

The general procedure for six steel specimens of an average hardness runs about as follows: First, the specimens, after mounting, are placed into the holders with about ⅛ inch extending beyond the edge of the holder, and clamped by the set screws so that the surface of the specimens to be ground is nearly parallel to the surface of the holder. The cast iron lap, if the specimen is very rough,

is charged with a paste of purified kerosene and M303.* After the lap has been placed on the machine the paste is smoothed out by means of hard steel loaders. This action of the loader leaves a uniform distribution of the grinding paste. The specimens are then placed on the lap and the flow of kerosene from the dropper is

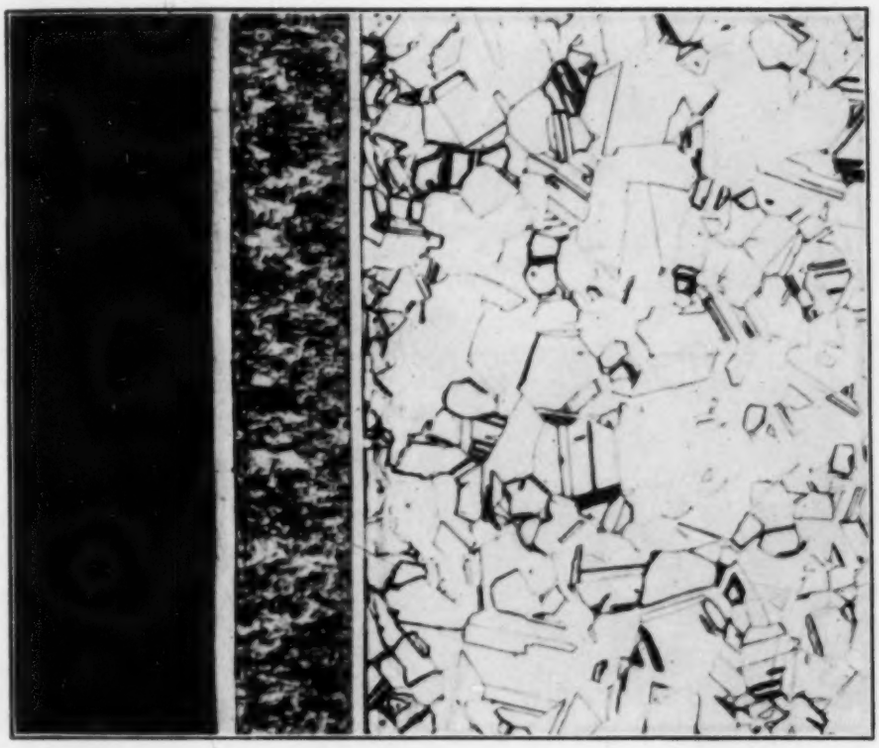


Fig. 6—Photomicrograph of Electroplated Brass Bar Etched with Ammonium Persulphate. × 200. This Shows the Retention of Sharp Edges of Adjoining Metals.

started with the speed of about two drops per second. The grinding is continued for about five minutes, after which the specimens and lap are thoroughly cleansed with kerosene and made ready for the next grinding operation. The compound used in the next grinding operation is M305,* and this step takes about five minutes. In grinding, weights may be used to speed up this operation without endangering the specimens. After these two grinding operations, the polishing starts and usually takes about three or four different grades of levigated alumina. A lead lap is used for this part of the cycle and the kerosene is applied by hand, using a small oil can to keep the lap lubricated. When loading the lead laps, the paste made of purified kerosene and levigated alumina should be smoothed out by means of

*Products of American Optical Company.

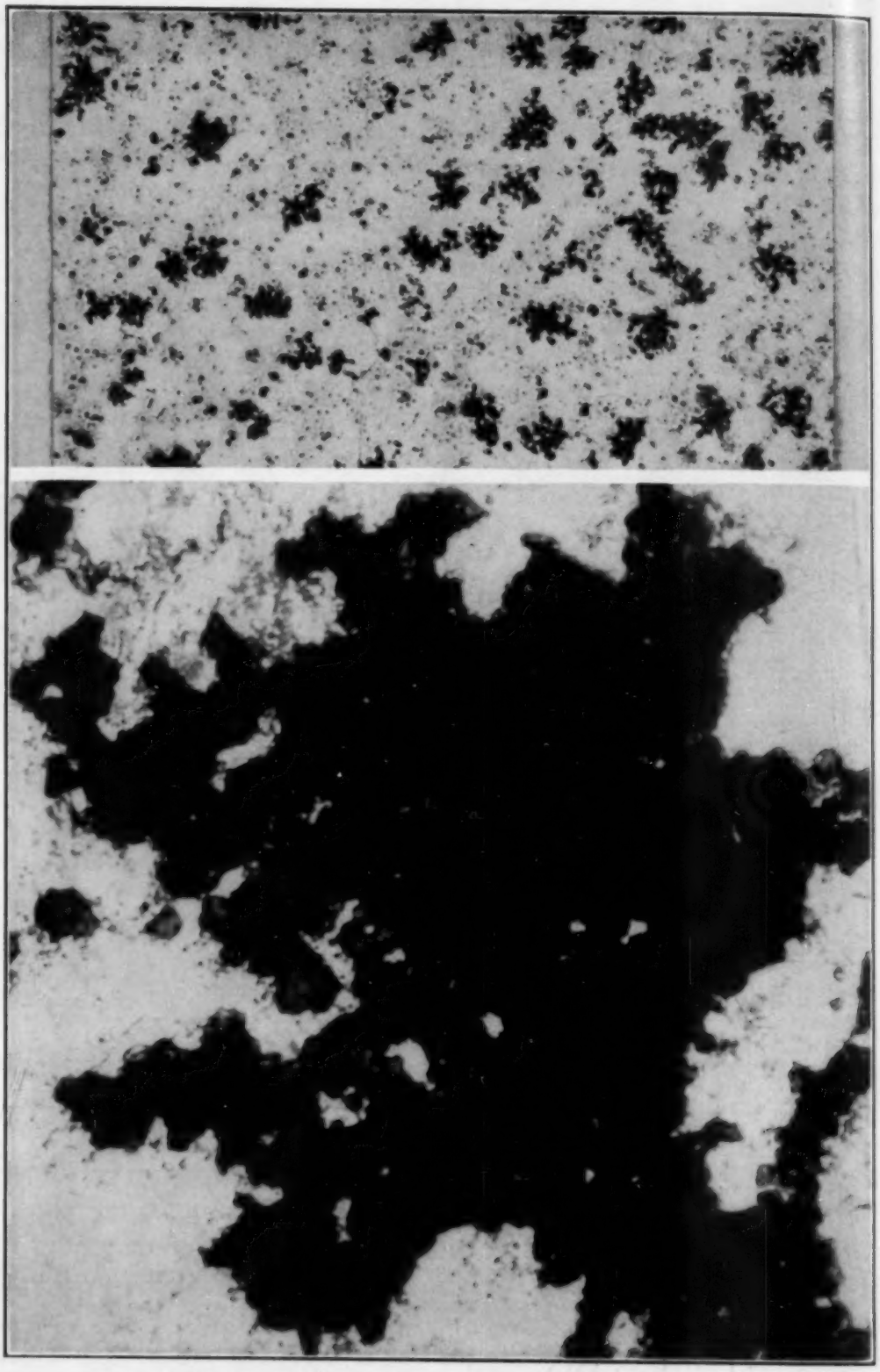


Fig. 7—Photomicrograph of Malleable Cast Iron, Nital Etch. × 50.
Fig. 8—Photomicrograph of Malleable Cast Iron, Nital Etch. × 1000.

the loaders for a longer period of time. This insures one of a very uniform distribution of the compound and shortens the polishing time to about ten minutes per lap.

The operator in using the above procedure will undoubtedly vary it to conform with the work he is doing.

In polishing specimens, the nearer that one can approach an optically flat surface the more accurate the results and the greater



Fig. 9—Photomicrograph of Gray Cast Iron, Unetched. × 50.
Fig. 10—Photomicrograph of Gray Cast Iron, Unetched. × 500.

the ease of photographing. The flatness of a cast iron specimen is shown in Fig. 3. This photograph was taken with monochromatic light having a wave length of 0.000546mm. In this photograph the distance between each band is one-half of a wave-length or 0.000273mm. If the specimens were optically flat the bands would be parallel and straight.

Some of the results obtained from this method of polishing are shown in Figs. 4-10. It should be noticed that the inclusions in Figs. 4 and 5 are not pulled out, and also in Figs. 7 to 10 the graphite particles are still intact with their parent metal. Fig. 6 shows how

it is possible to obtain sharp edges when different metals are electro plated upon each other. The nickel plate next to the brass bar is 0.0003 inch in thickness.

The author wishes to thank H. W. Schwartz, manager of research of National Malleable and Steel Castings Company, for the cast iron specimens used in preparing this paper. He also wishes to acknowledge the assistance of W. J. Wrighton, chief metallurgist of the American Optical Company, and Lawrence Litchfield, laboratory assistant, whose help in developing the polishing technique was invaluable.

DISCUSSION

Written Discussion: By L. R. vanWert, metallurgist, Leeds and Northrup Co., Philadelphia.

To this reader, Dr. Jarrett's paper is, in the first place, a reminder that substantial progress has been made in metal-lap polishing technique since he first observed Dr. Graton's early work on ore minerals in the middle 1920's. Much of the progress that has been made since that time has, in fact, been due to the continued work of Dr. Graton and his co-workers in Economic Geology at Harvard, and—to the small extent that his technique has been applied to microscopical metallography—to certain former students of physical metallurgy at Harvard, as Dr. Jarrett, who has an unusual opportunity to observe the development of Dr. Graton's machine and technique.

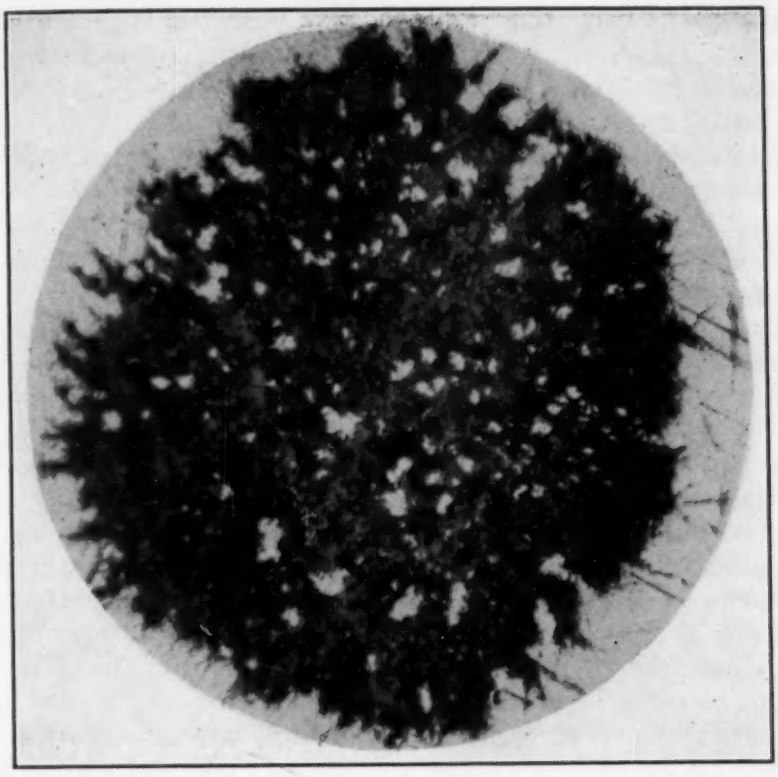
More specifically, I find interest in the author's paper because of what he has been able to accomplish for metallurgists in the field of automatic polishing on metal-lapped disks, namely: an unusual flatness of field, the absence of relief polishing effects in heterogeneous alloys made up of phases of widely varying hardness, and the relative freedom from scratches.

It might be of interest to some, if the author would give the name of the manufacturer of his polishing machine.

Written Discussion: By H. L. Anthony, III, research metallurgist, The Midvale Co., Nicetown, Philadelphia.

While the Geology Department of Harvard University, Cambridge, Massachusetts, has been utilizing a method similar to that described by the author for polishing mineral specimens, the commenter believes that this is a new approach in the polishing technique of metal specimens. While the time of polishing is far too long for commercial production, it lends its application to research especially in the field of nonmetallic inclusions where metal flow and vibration are present in the paper and cloth methods.

The accompanying photomicrograph is of malleable cast iron produced at 650 degrees Cent. for 248 hours. It has been polished similar to the method used by the author. While the method was not as refined as the one described in this paper, existing scratches on the outside of the nodule of graphite are very evident.



However, the internal structure of the graphite nodule in this photomicrograph is similar to the author's Fig. 8 in that the small particles of ferrite are exhibited. Ordinarily the paper and cloth laps would have caused the graphite to flow and the small particles of ferrite would never have been noticed.

It has been a pleasure to review the paper and I am sure the author will ascertain a method in the near future for eliminating the small scratches he mentions in this method.

Written Discussion: By C. W. Mason, professor, chemical microscopy and metallography, Cornell University, Ithaca, N. Y.

Scientific investigation of surfacing processes is certainly necessary, for improvements both in technological operations (polishing, buffing, etc.) and in microscopical preparations, technique, in which the surfacing procedure is one of the most important determinants of realiable observation.

The author uses the terms "ground" and "polished" as if they represented different kinds of surfacing processes, whereas with microscopically fine abrasives the difference is of degree. The extremes might be thought of as planing contrasted with burnishing action of the surfacing medium, but of course both these actions exist. A third type of surfacing action occurs when the abrasive particles roll, and exert what is essentially a chipping and indenting action, as distinguished from their planing and flowing action when the grains are more or less anchored in cloth or soft metal laps. This third type of abrasion is probably minor in most metallographic surfacing, but is of major importance in the surfacing of brittle minerals and in grinding glass.

Intermediate effects may occur if the abrasive is carried on a relatively hard smooth lap.

It would be helpful if investigations of surfacing on metal laps gave more consideration to the above three modes of approximating a plane surface, and attempted to analyze the way in which each one might be controlled. Certainly the nature of the lap and of the specimen, the mechanical properties of the abrasive, the lubricant, and the speed are the most important factors, but any or all of these factors may depend on as complex theory as that now known to govern the lubrication of bearings.

For the above reasons an empirical study, however effective its results on certain materials, can contribute little to the broader knowledge of surfacing processes. Even a statement of the actual initial and working sizes of the abrasive (as well as the manufacturer's number or the term "levigated") would be a step in the right direction. The pressure per unit area of the specimen, and the actual surface speed would also be easy of determination. Without these, and other more complex data, the work can be judged only by the specimens produced. It is unfortunate that Figs. 8 and 10, although indicating little rounding of the edges of the metallic matrix (oblique illumination would be a better test of this) do not give the impression of smooth retained graphite, which in photographs having normal contrast appears gray, not black.

It might be pointed out that macroscopic planeness, as indicated by interference fringes at ×5 (Fig. 3), while important in lapping operations for mirrors, prisms, and lenses, is much less significant in metallography than microscopic smoothness over the field examined. Local microscopic undulatons would not be revealed unless the fringes were observed at the magnification to be used, as has been done by Hoare and Chalmers.[3] The apparent roughness of the fringes pictured points to lack of microscopic planeness, even though the specimen as a whole is flat.

The methods of preparation of abrasives and of the specimen are not stated in sufficient detail to enable another worker to duplicate them. If equally good results may be obtained using any variations comprised within the vague directions given, there appears to be little presented that is specifically novel.

Oral Discussion

CARL L. SHAPIRO:[4] Dr. Jarrett's paper is a distinct advancement to our knowledge of polishing and, although the basic principle has been applied by others, the technique of polishing has been greatly improved by him. This improvement not only rests in the polishing powders but also in the polishing machine proper. However, I would like to ask Dr. Jarrett a few questions, namely: (1) Is the fine polish attained due to the uniformity of the abrasive powders or due mainly to the improved machine construction and (2) can the speed of polishing be increased by increasing proportionately the revolutions per minute of the head and lap in the same ratio of 200 to 90 as is used now?

[3] *Journal*, Iron and Steel Institute, Vol. 132, 1935, p. 135.

[4] Consulting engineer, Syracuse, N. Y.

O. E. HARDER:[5] It appears that even in this automatic polishing there is a great deal that depends upon the individual. I have not polished metallographic specimens for eight or ten years, but I have had occasion to look at a good many that have been prepared and to look at the results obtained and observed that probably the most frequent defect is over-polishing.

These fellows who polish and polish are I think, like the cook who was boiling eggs. She cooked and cooked them in an effort to get soft boiled eggs. That is what happens to these metallographical specimens—they keep polishing and polishing and they will not flatten. What they are doing is roughtening them more and more. It is my experience that if those fellows would use about a fifth and in some cases only a tenth of the polishing time and keep a flat surface, they would get a very much better preparation. I refer to polishing on cloth.

W. H. SWANGER:[6] I would like to ask for further information on a question brought up in one of the previous discussions of Dr. Jarrett's paper. Does anyone here care to express an opinion as to whether or not increasing the speed of rotation of the polishing wheel would result in more rapid completion of the polishing operation?

Author's Reply

The author is indeed grateful to those who have discussed this paper, and the number of discussions offered indicates the interest that is centered upon the preparation of metallurgical specimens.

It is most pleasing to note that others such as Dr. Anthony, have also observed similar results in cast iron specimens. The author is inclined to agree that this method is too long for commercial production, but it is his hope that from investigations now going on the polishing time will be shortened and also an improvement in technique brought about.

Dr. vanWert is correct in saying that this type of polishing was first applied to minerals and the author, bearing this in mind, has described a method basically similar, but with improvements and modifications that make it applicable to metal polishing.

In reply to Mr. Swanger's remarks the speed of the machine of course is important. If you use too high a speed there is a tendency for the specimens to be thrown to the outside of the lap, producing a very high center. This is very pronounced when using a speed of 250 r.p.m. When using a speed less than 200 r.p.m. the grinding and polishing operations are slowed up considerably. Dr. Shapiro has brought up a very important point about polishing powders. We have found that the uniformity of the powder is extremely important. If there are a few large particles in the fine powder deep scratches will be produced and the object of the fine powder will be destroyed. The uniformity of the powder and the construction of the machine must be correct to obtain good results. There is no advantage in increasing the speed of the machine in the same ratio that is now used.

With reference to Dr. Mason's remarks, the author wishes to state that

[5]Assistant director, Battelle Memorial Institute, Columbus, Ohio.
[6]Metallurgist, National Bureau of Standards, Washington, D. C.

the term "ground-polished" is justified because it certainly is not a true ground surface, but it approaches the characteristics of a true optical surface. In regard to the difference between a ground and polished surface, even experts in the optical field still disagree and it is a perennial topic of discussion.

The author wishes to stress again that he did not intend this to be a theoretical paper, but rather to be a general outline of an improved method for the preparation of metallurgical specimens for microscopic examination. In the grinding operations, the sizes of the particles are of less importance than the shape of the grinding particles and their uniformity. The M303 and M305 are American Optical Company catalog numbers and are widely used throughout the world and have the respective average sizes of 800 and 3200 mesh. The sizes of the polishing compound have not been determined. As was stated in the paper, they were produced from Norton's levigated alumina.

In Figs. 8 and 10, the appearance of the graphite being black or gray is a matter of photographic technique and of personal preference.

In the reference to Hoare and Chalmers, there are deep holes of many wave lengths to be measured in their material and, in consequence, high magnification is necessary. This high magnification is necessary because the included angle is so sharp and the fringes consequently very close together. In Fig. 3 of the author's paper there are no such sharp holes present, and a higher magnification covering a smaller area would only show one band, with possible irregularities very much less than a width of a band.

In determining the kind of sizes of abrasives to be used in this method, considerable research had to be done. Certain particle sizes and structures are necessary for good results upon metallurgical specimens. In polishing minerals there is a wider tolerance of compounds than may be used. The author tried a large number of compounds, such as carborundum, corundum, levigated alumina, tin oxide, etc., and found that the compounds mentioned in the paper gave the best results. It was the intention of this paper not to describe this method in exact detail. As previously stated, another operator may vary this detail procedure to suit his own conditions. The fact remains that in the literature no such results have been shown and therefore the author believes that this method has some merit and may prove to have considerable value in the preparation of metallurgical specimens. Such has been the writer's own experience in its practical use.

There appears to be some doubt about the possibilities of automatic polishing machines. I do believe, however, that there is a time coming when polishing metallurgical specimens will be a simple routine rather than an art. As was stated, the polishing of specimens is an art, and this so-called art is brought about by the fact that the human element plays an important part in the polishing of specimens. In the near future I think that an automatic polishing machine will be on the market that will reduce the effect of the human element and tend to standardize the polishing of metallurgical specimens.

A METALLOGRAPHIC APPROACH TO THE STUDY OF THE SENSITIVITY OF STEEL TO COLD WORK

By H. K. Work and S. L. Case

Abstract

This paper presents results of a metallographic study on a number of steels displaying considerable variation in their sensitivity to cold work and their aging characteristics. The sensitivity of these steels was measured by a work-brittleness test; their aging behavior was evaluated by means of damping capacity tests. The metallographic examination utilized a modification of Fry's microetching reagent and was made on broken tensile test specimens annealed at 600-800 degrees Fahr. (315-425 degrees Cent.). It was shown that the number and character of strain lines produced by the etching technique are parallel to work-sensitivity and aging tests. This method of examination is applicable to low as well as medium carbon steel and it can be used on thin gage materials and small specimens.

Introduction

THE suitability of a steel for any particular application depends on many factors. Not the least important of these are the variations from heat to heat which are not explained by ordinary chemical analysis. In former years it was customary to consider these differences as normal commercial differences. In recent years, however, there has been a determined effort to understand them and use them to the advantage of the steel fabricator. Studies of grain size, gases in steel, hardenability, heat treatment, and sensitivity to cold work exemplify this effort. The study described here was directed toward finding a simple metallographic test for the prediction of the sensitivity of steel to cold work.

The term "work-sensitivity" was first employed by H. W. Graham (1)[1] to signify "a characteristic degree of reaction of steel

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twentieth Annual Convention of the Society held in Detroit, October 17 to 21, 1938. Of the authors, H. K. Work is manager of research and development, Jones and Laughlin Steel Corporation, and S. L. Case is metallurgist, research and development division, Jones and Laughlin Steel Corporation, Pittsburgh. Manuscript received July 25, 1938.

to cold work." Differences in work-sensitivity manifest themselves in the degree of embrittlement and aging after cold work. This variation in response to cold work is measured by a work-brittleness test briefly described in another paper by the same author (2). A tapered round bar 0.450 inch on one end and 0.475 inch on the other end is prepared. The total length of the tapered portion is 10 inches. This specimen is drawn through a 0.450-inch die. The result is a gradual increment of cold work from zero on one end of the specimen to 10.3 per cent reduction of area on the other end. The cold drawn specimen is notched with a regulation Izod notch at 1.1-inch spacings and broken on an Izod impact machine, thus furnishing eight points for a work-brittleness curve from a single specimen, the increment of cold work from point to point being equivalent to 1.2 per cent reduction of area. It was pointed out that the characteristic response of a given heat to cold work is apparently independent of chemical composition, so far as common elements are concerned, and that it cannot be readily predicted from static tests or grain size. The general concept of work-sensitivity and the application of damping capacity measurement to evaluation of sensitivity and aging characteristics of steel has been amplified in recent articles by S. L. Case (3), (4). The present paper gives results of metallographic studies of a number of steels on which the work-sensitivity was determined by means of work-brittleness tests, and aging characteristics were investigated by damping capacity measurements.

The purpose of this metallographic study was to develop a test which could be substituted for work-brittleness and aging tests on thin gage material where the dimensions do not permit the preparation of work-brittleness or damping capacity test specimens.

Work-Sensitivity and Damping Capacity Aging Tests

Table I shows the chemical composition of five heats of steel used to illustrate this study. Both heats 88225-2A and 88225-R are of Bessemer origin, while heats C-355, C-357, and C-358 were made in a laboratory induction furnace. The work-brittleness tests on these heats are shown graphically in Fig. 1. The aging characteristics of these heats are illustrated by means of damping capacity tests on Figs. 2 and 3. From the work-brittleness curves it is evident that heats 88225-2A and C-357 have a very low work-sensitivity, i. e.,

Table I
Chemical Composition of Steels Used for Strain Line Studies

Identification	Per Cent				
	Carbon	Manganese	Phosphorus	Sulphur	Silicon
88225-R	0.10	0.34	0.095	0.053	0.065
88225-2A	0.09	0.37	0.095	0.055	0.029
C-355	0.14	0.54	0.010	0.030	0.180
C-357	0.12	0.54	0.009	0.031	0.230
C-358	0.19	0.46	0.007	0.032	0.200

Steel 88225-R was semi-killed; all the other steels were fully killed.

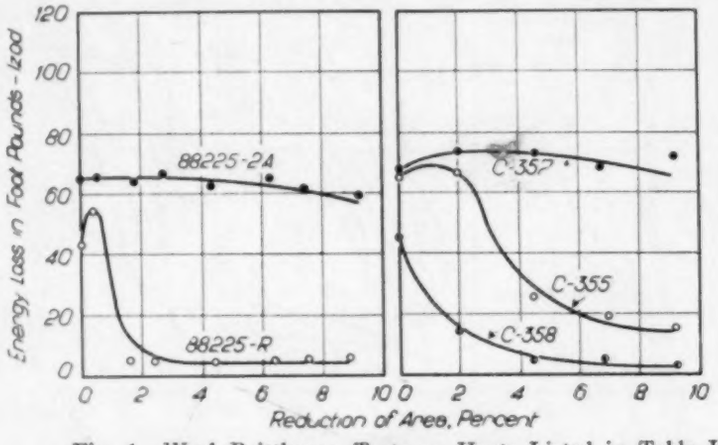


Fig. 1—Work-Brittleness Tests on Heats Listed in Table I. Steels 88225-2A and C-357 Show a Low Order of Work-Sensitivity; Steels 88225-R and C-358 are Very Sensitive; Steel C-355 is Intermediate. Test Specimens were Normalized at 1650 Degrees Fahr. Previous to Machining.

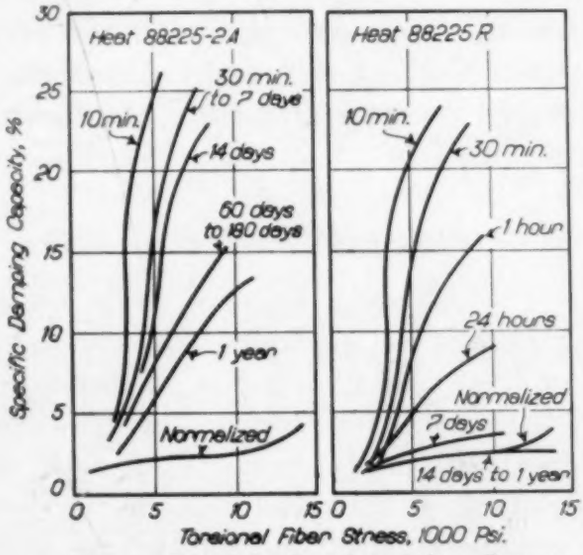


Fig. 2—Damping Capacity Aging Curves on Heats 88225-2A and 88225-R. 88225-2A has a Low Aging Rate, While 88225-R is Rapidly Aging, Showing Appreciable Strain Aging in 1 Hour After Cold Working. In 24 Hours it Aged More than 88225-2A Aged in 1 Year. Tests were made on Specimens Normalized at 1650 Degrees Fahr. Previous to Machining.

they show little embrittlement under cold work up to 10 per cent reduction of area. Heats 88225-R and C-358 are very sensitive to cold work, while heat C-355 is of intermediate work-sensitivity. The aging characteristics of these heats, as evident from their damping capacity curves, parallel their work-sensitivity ratings. Heat 88225-2A shows very little aging in 14 days; heat 88225-R was almost

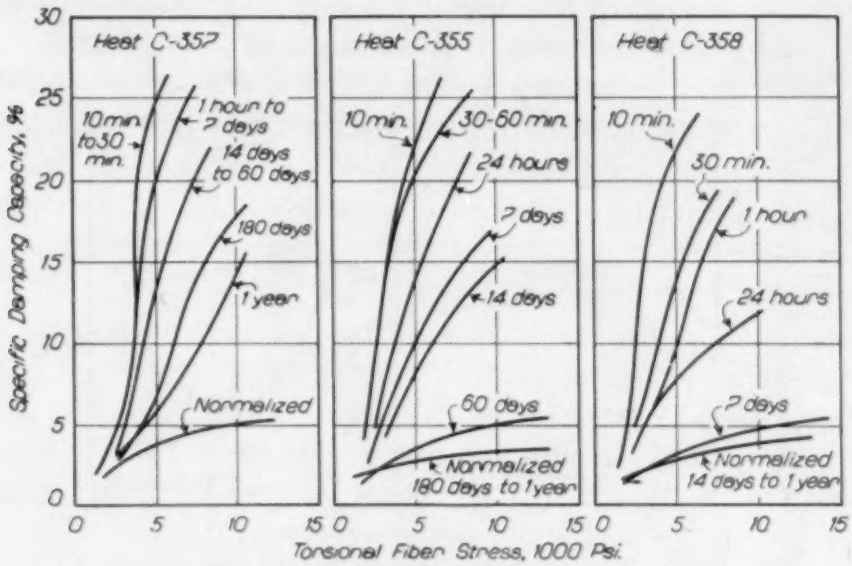


Fig. 3—Damping Capacity Aging Curve on Heats C-357, C-355, and C-358. Steel C-357 has a Low Aging Rate, C-358 a High Aging Rate, and C-355 is Intermediate. Tests were made on Specimens Normalized at 1650 Degrees Fahr. Previous to Machining.

completely aged in this time interval, and shows perceptible aging in 30 minutes. Heats C-357, C-355, and C-358 display aging differences, having roughly the same relationship to each other as their work-sensitivity ratings.

Macroetching for Strain Lines

Since A. Fry (5) published results of strain line etch investigations, his etching method has generally been considered a desirable approach to the study of cold deformation. Other investigators (6), (7) have shown that strain lines developed by this etching procedure seem to be associated with notch toughness and aging characteristics. Their work was based on macroetching, and, as Jevons (6) has established, the etching requires periods as long as 100 hours to bring out finer distinctions, and even at that many steels apparently fail to develop strain figures under a macroetch. Like Luders lines, strain lines developed by a macroetch appear only in portions of the

specimen overstrained just slightly above the yield point, and are brought out only in low carbon steels. The nature of the strain lines for the present remains a conjectural subject. Fry associated them with oxides of iron and silicon. Köster attributes them largely to nitrogen. According to Köster (8), this is the mechanism of their formation. Nitrogen precipitates out very sluggishly, so that under normal cooling conditions a supersaturated solid solution is formed. When such material is cold-worked and then annealed at a temperature in the neighborhood of 500 degrees Fahr., preferred precipitation of nitrogen takes place in the strained zone. The same reasoning could apply to iron oxide or any other constituent which imparts to steel aging characteristics. Recent researches (9), however, point to the conclusion that while oxygen enhances the effect of nitrogen, in the complete absence of nitrogen, oxygen does not lead to formation of strain lines.

Microetch Tests for Strain Lines

While macroetching for strain lines has been used rather frequently in the study of steel behavior, very few references are available on the significance of microetching methods. It is well known, however, that strain lines can be developed in a cold-worked steel specimen by various etching reagents. A nital etch often brings them out, but Fry's etching reagent generally shows more consistent results. A comparison of the two etching methods is shown in Figs. 4 and 5. The nital etch brought out very few strain lines, while Fry's reagent developed a large number of them in the same specimen. Whether or not the strain lines developed by both reagents are qualitatively identical is a debatable question. That a qualitative difference between them may exist is indicated by the fact that quenching from above the upper critical temperature previous to cold working accentuates strain lines developed by a nital etch, while it seems to inhibit strain lines developed by Fry's reagent.

It was found that if, previous to etching with Fry's reagent, the cold-worked specimen is annealed at a temperature of 600 to 800 degrees Fahr., the strain lines seem to reach a maximum intensity in both quality and quantity. The results, however, were difficult to follow due to the tendency of copper to plate out of the solution and obscure the general picture. A modification of this reagent was arrived at and was found to give more consistent and reproducible

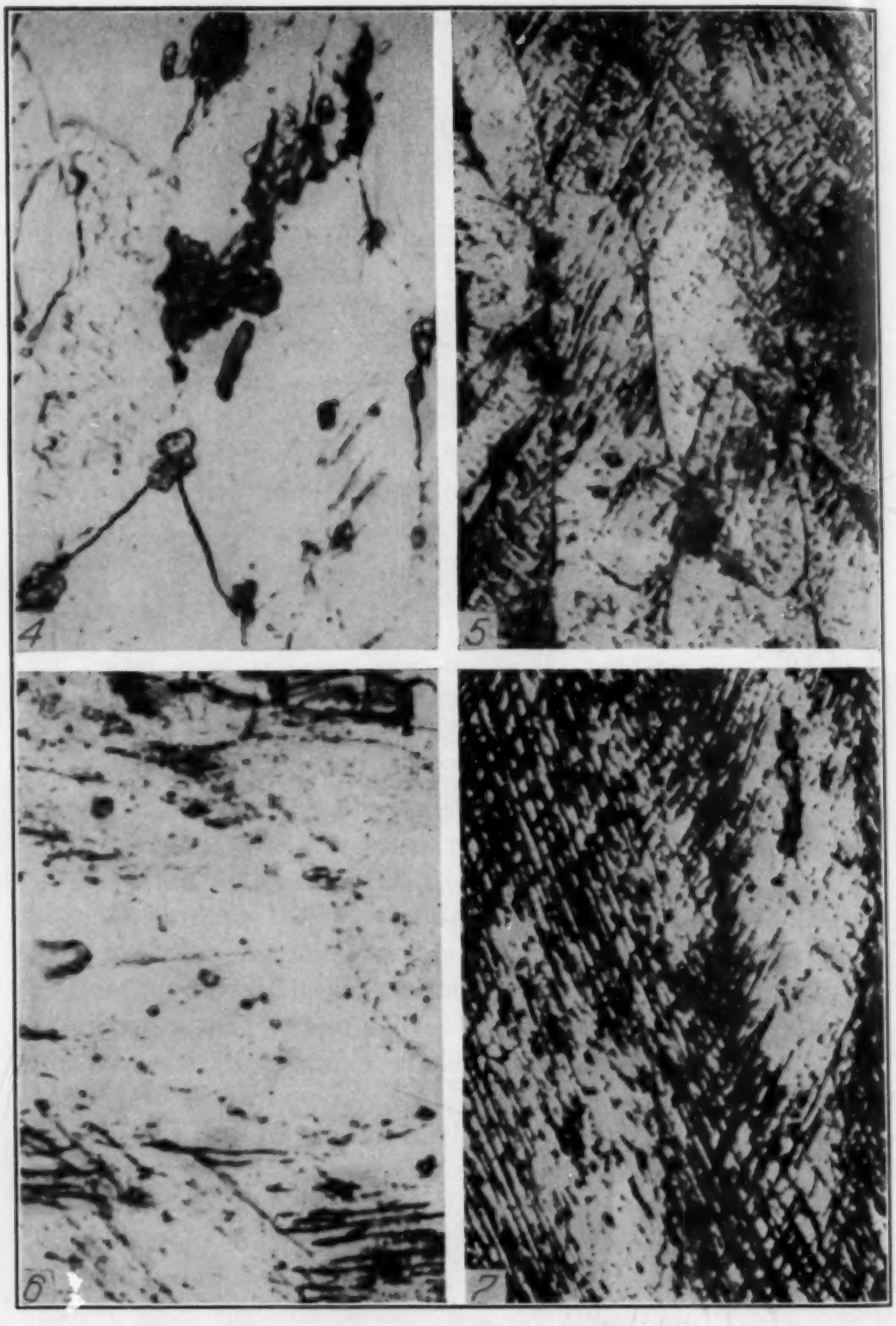


Fig. 4—Strain Lines Developed in Low Carbon Steel by Etching with 4 Per Cent Nital. Test Specimen Annealed for ½ Hour at 700 Degrees Fahr. × 1000.

Fig. 5—Strain Lines Developed in the Same Specimen as Shown in Fig. 4 by Etching with Modified Fry's Reagent.

Fig. 6—An Insensitive Heat. Specimen Taken from Broken Tensile Test at Point of Fracture. Annealed at 700 Degrees Fahr. and Etched in the Reagent, Described in Table II.

Fig. 7—A Sensitive Heat. Specimen Taken from Broken Tensile Test at Point of Fracture. Annealed at 700 Degrees Fahr. and Etched in the Reagent, Described in Table II.

results. The comparison of Fry's original reagent and etching technique as well as that of the modified reagent is shown in Table II. In the preparation of the specimens various types of cold work, such as tension, compression, bending, and torsion, were tried. It was found that ordinary broken tensile specimens, if examined near the break, fully answered the purpose of the test, since the amount of cold work in the necked portion is sufficient to bring out essential differences in the response of various steels to the microetching procedure. Previous to breaking, the tensile specimens are subjected to a normalizing treatment at 1650 degrees Fahr., to eliminate the effects of any previous cold work or internal stresses. The examination described below was made on the longitudinal section of the tensile specimens which, after pulling the test, were annealed at 700 degrees Fahr. (370 degrees Cent.) for ½ hour, polished and etched repeatedly, as explained in Table II.

Table II
Etching Reagents and Etching Practice Used in Strain Line Studies

	Fry's Reagent	Modified Reagent
Composition		
Hydrochloric Acid	40 cc.	11 cc.
Water	30 cc.	..
Cupric Chloride	5 grams	4.5 grams
Ethyl Alcohol	25 cc.	25 cc.
Preparation of Specimen	Anneal for ½ hour at 400-500° F.	Anneal cold-worked specimen for ½ hour at 600-800° F.
Etching Procedure	Etch for 10 seconds	Give preliminary etch in nital to show pearlitic grains. Etch for 4 seconds in modified reagent. Repeat etching until the intensity of strain bands stops increasing.

Microetch Tests with Modified Fry's Reagent

Results of the metallographic examination of the heats described previously are illustrated in Figs. 6 to 10 inclusive. As had been anticipated, work-sensitivity and aging characteristics of these steels are indicated qualitatively in the strain line micrographs. The two Bessemer heats shown in Figs. 6 and 7 give a particularly striking example. On the insensitive heat 88225-2A comparatively few strain lines are present and only in a few favorably situated grains, the rest of the grains being practically free of strain bands. On the sensitive heat 88225-R the strain lines show a regular geometric pattern, indicating slip or precipitation along at least two planes and covering practically the entire ferrite area in each grain. The induction fur-

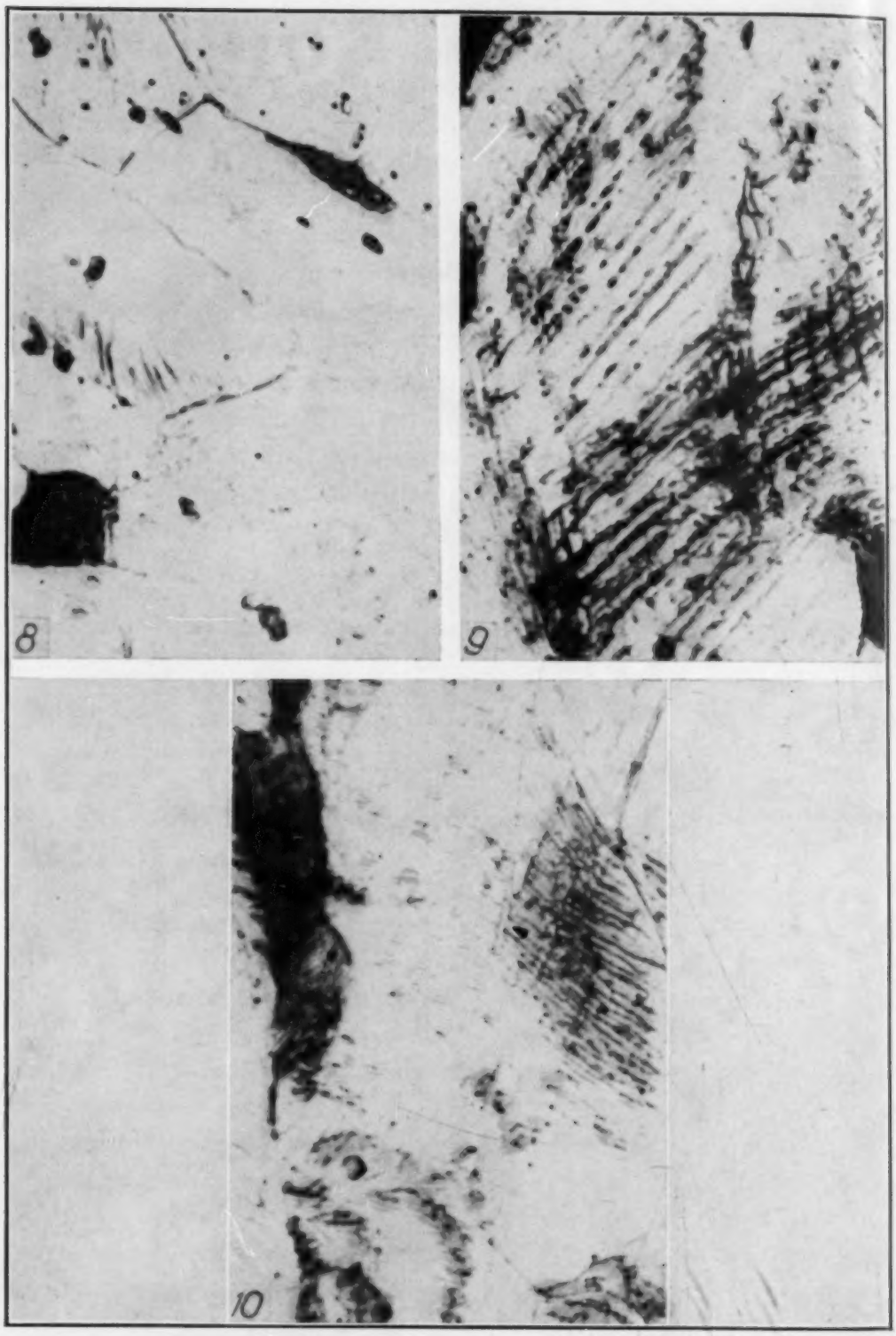


Fig. 8—An Insensitive Heat. Specimen Taken from Broken Tensile Test at Point of Fracture. Annealed at 700 Degrees Fahr. and Etched in the Reagent, Described in Table II.

Fig. 9—A Sensitive Heat. Specimen Taken from Broken Tensile Test at Point of Fracture. Annealed at 700 Degrees Fahr. and Etched in the Reagent, Described in Table II.

Fig. 10—A Heat of Intermediate Sensitivity. Specimen Taken from Broken Tensile Test at Point of Fracture. Annealed at 700 Degrees Fahr. and Etched in the Reagent, Described in Table II.

nace heats tell a similar story; very few strain lines are evident on the insensitive heat C-357, a maximum on the sensitive heat C-358, and the intermediate heat C-355 occupies a corresponding position in the occurrence of strain lines.

Results shown in Figs. 6 to 10 are typical of a large number of other heats examined by this method. In associating the strain line etch tests with work-sensitivity and aging characteristics of steel, it is of interest to note that, as a regular occurrence, the strain lines developed in work-sensitive steel cover the entire ferrite grain and extend a considerable distance from the break in a tensile test piece, while in an insensitive steel they are generally found only in certain favorably oriented grains and seldom extend throughout the entire grain; they are also limited to an area in the immediate vicinity of the break. They can be developed in any hypoeutectoid work-sensitive steel containing free ferrite. It is, however, important to bear in mind that a certain amount of care is essential in carrying out the etching procedure. Overetching tends to darken and stain the specimen; underetching may fail to bring out the maximum number of strain lines in a particular grain. In general, repeated etching should be continued until there is no further increase in the number of strain lines.

The microetch method offers a new approach to the study of work-sensitivity and aging characteristics of steel. The practical value of such a test lies in its ready applicability to thin gage materials, such as wire and strip, which do not permit use of certain of the more selective physical tests for determination of these properties. The steels used as illustrations in this paper were of the killed and semi-killed types. The application of the test to heterogeneous products, such as rimmed steels, is now being investigated.

Summary

1. A new metallographic index of sensitivity of steel to cold work and its aging characteristics is described.

2. Strain lines, produced in cold-worked steel by a modification of Fry's etching reagent, are apparently associated with work-sensitivity and aging characteristics of steel.

3. This method of evaluating work- and aging-sensitivity can be used on low as well as medium carbon steel. It is also applicable to thin gage materials and small specimens on which work-brittleness and damping capacity tests cannot be made.

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DISCUSSION

Written Discussion: By Oscar E. Harder, assistant director, Battelle Memorial Institute, Columbus, Ohio.

The authors of this paper have made an interesting contribution in their correlation of the work-sensitivity of steels with impact resistance, damping characteristics, and response to a modified Fry's etching reagent.

As the authors ably point out in their introduction, much progress has been made in the finer points which characterize steels. In this line it seems hardly adequate to simply say that a steel was semi-killed or fully killed. There was a time when silicon was largely relied upon to kill the heat but at the present time the steel may be killed by silicon, aluminum, titanium, or zirconium, or combinations of these elements. It is also of importance to know at what time in the steel making process the metals were added for killing the heat.

I believe Dr. Work in presenting the paper mentioned that certain of these steels were killed with aluminum. In that case, it is also of some interest to know the amount of aluminum added and whether the aluminum added was all or practically all converted into alumina or whether metallic aluminum was retained in the steel.

It might be of interest to those engaged in studying work-sensitivity and aging of steels to make reference to the research conducted at Battelle Memorial Institute, 1930 to 1932, and published by Samuel Epstein in Proceedings of A.S.T.M., Vol. 32, Part II, pages 293 to 374. In that paper there was shown to be a difference in the type of steel (Bessemer, duplex, open-hearth, Izett, etc.) regarding its sensitivity to cold working, as in punching holes, and as in

compressing the specimens various amounts and then testing them in impact. The effect of testing temperature also showed that there was a difference depending upon the type of steel and how it was made.

The relations which the authors have found between damping capacity and other properties of steel are interesting and should be valuable in further research work along this line.

I would like to know whether or not the authors have found a correlation between the nitrogen content of the steels and their sensitivity?

Oral Discussion

W. A. SCHUMACHER:[1] I would like to ask the authors if any work has been done on the checking of the sensitivity of S.A.E. 1065 hardened tempered steel to cold work.

I. A. ROHRIG:[2] I should like to ask the authors if they have tried any of these tests on steels which have been strongly deoxidized with aluminum. Then I note on the first slide shown that the silicon was relatively low in the heats that were fully killed and I believe if the silicon were higher the tendency of sensitivity to cold work would be eliminated. I have noticed a condition similar to this, such as the strain lines that were shown on some of the earlier 18-8 alloys in which the carbon was rather high. It was possible to produce conditions very similar to the strains.

W. H. SWANGER:[3] I would like to ask the authors a question concerning the results of their Izod tests on the work-hardened steels. The curves show distinct differences for the several steels. It is known also that with many steels, similar differences are obtained on specimens from the same steel, if the Izod, or Charpy, tests are made over a sufficiently large range of temperature. Were effects of different temperatures of test correlated with the differences in the materials shown in the paper?

GEORGE F. COMSTOCK:[4] What is the maximum carbon content of the steel to which you think this metallographic test could be applied?

H. F. KAISER:[5] I would like to ask Dr. Work if, in the Izod specimens giving graded increments of the cold work, he found any correlation in the number and distribution of strain lines in the cold work. That is, just how did the concentration of the strain lines increase with the degree of cold work?

C. D. COXE:[6] Is my understanding correct that sensitivity to cold work increases as susceptibility to aging increases? If so, is it safe to assume that the so-called stabilized or non-aging steels will be immune from sensitivity?

RALPH W. E. LEITER:[7] The work-brittleness curves of the several steels obtained by plotting Izod-impact test values against per cent cold reduction shows in some instances a distinct increase in ductility with a small amount of cold work. The authors have made no analysis of this peculiar phenomenon. I should like to ask if there is any relation between this increase in ductility and sensitivity to cold work.

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In our static tensile testing we find that fully annealed low carbon steel shows a marked decrease in ductility above a certain critical rate of deformation. Stretcher strains start at several points and before they can traverse the test piece fracture occurs in one of the parts first to deform; the reason being that the lower yield point is higher than the tensile strength. This critical rate of deformation has been found to be as low as 40 inches per inch per minute for one steel. In impact testing we would expect this critical rate to be exceeded in all cases.

A small amount of cold work markedly lowers the yield point and causes deformation to occur simultaneously in all parts of the test piece. More metal is deformed so that the energy required for fracture is greater than in the case of fully annealed steel.

I. A. ROHRIG: One thing more comes to my mind. I wonder if the authors feel that at the present time their work would in any way show that this study of sensitivity to cold work could be in some way related to creep rates, or the sensitivity to creep?

Authors' Reply
(Dr. Work)

Replying to Mr. Schumacher's question concerning the S.A.E. 1065 steel, both work-brittleness and damping tests have been used to check the sensitivity of this material. The metallographic test cannot be used because the material contains no free ferrite.

With reference to Mr. Rohrig's question on the use of aluminum for deoxidation, it has a very marked effect on sensitivity, although I would like to point out definitely that the deoxidation practice is not the only factor. In other words, there is the question of what you are deoxidizing as well as the deoxidizing procedure. With reference to the Bessemer heats, the one that was insensitive was deoxidized with aluminum, while the sensitive heat was silicon capped. In the case of the induction furnace heats, the insensitive one was aluminum and silicon-killed and the other two were silicon-killed. There was considerable difference between the intermediate sensitive steel and the very sensitive one. The killing was the same, but there was a difference in the material itself.

Replying to Mr. Swanger's question on the effect of temperature on the impact tests, it is possible to secure a general picture of sensitivity by making impact tests over a range of temperature, but we have found the work-brittleness test more convenient for our purposes because it gives a quantitative measure of the effect of cold work on the impact strength of the steel.

With reference to Dr. Harder's question on the effect of nitrogen, the total nitrogen on the two Bessemer heats, which differ so greatly in sensitivity, was practically identical.

Replying to Mr. Comstock's question about the maximum carbon content, this metallographic test may be used on any steel containing free ferrite.

With reference to Mr. Kaiser's question about the effect of the variations in the strain lines developed in the work-brittleness test specimens, our metallographic tests were made on tensile test specimens—not Izod specimens.

Mr. Coxe raises a question about the relationship of sensitivity versus

aging. We definitely feel that the sensitivity and aging are related phenomena; in other words insensitive steels are non-aging. As a matter of fact, we consider aging a phase of the general subject of sensitivity.

Replying to Dr. Leiter's question regarding the rise in the work-brittleness curve noted at small amounts of cold work, we do not always get this and I am not certain whether or not it is significant. It may possibly result from a lack of precision in the Izod test itself.

With reference to Mr. Rohrig's question on the relation of sensitivity to creep, we have not attempted to correlate the two phenomena.

Replying to Dr. Harder's written discussion, I believe that his questions are already substantially answered in the reply to Mr. Rohrig's oral discussion. With regard to the suggestion that more data on the deoxidation practice be included, we feel that this does not tell the whole story and may actually be misleading. Therefore, since the paper deals primarily with a metallographic test rather than an attempt to explain the phenomenon of work embrittlement and aging, this information was intentionally excluded.

The authors wish to thank the various discussors of this paper for their kind interest in it. It is hoped that this paper will stimulate further work on this very intriguing subject.

METHODS OF PREVENTING SHATTER CRACKS OR FLAKES IN CARBON STEELS

By H. B. Wishart and A. N. Swanson

Abstract

High carbon steel purposely impregnated with hydrogen is highly susceptible to internal cracking, in the larger sections, when regularly cooled from rolling temperature. Advantage has been taken of this method to secure suitable steel for the study of these cracks or "flakes" in a convenient product, rails, in which the incipient ruptures are known as "shatter cracks." Methods have been developed to prevent shatter cracks in such sensitive steels.

The paper reports the temperature range during cooling in which the cracks form and the optimum cooling schedules which prevent the cracks. The study includes:

1. *Controlled or retarded cooling of the steel over several different ranges of temperature after the last rolling operation, and*
2. *Halting the regular cooling of the steel and holding at several approximately constant temperatures, below the transformation temperature and at and above 500 degrees Fahr., for a variety of intervals, prior to final air-cooling.*

Both schedules eliminate cracks. By the first method, an adequately retarded cooling applied after cooling to any temperature above about 400 degrees Fahr. suffices. By the second method, which is more effective for a given time cycle, a holding of only 1½ hours at 1000 to 1200 degrees Fahr. prevents cracks. Thus temperature and time interval are essential factors to be controlled and these in turn are determined by mass.

INTERNAL cracks, commonly known as flakes or shatter cracks, which form occasionally in the larger sections of high carbon steel during cooling have been intensively studied, but have not been completely explained. Analyses of the various manufacturing processes in steel making have, generally speaking, failed to show why some heats of steel are seemingly predisposed to this internal disrup-

Of the authors, H. B. Wishart is metallurgist, and A. N. Swanson is assistant chief metallurgist, Carnegie-Illinois Steel Corporation, Gary, Indiana. Manuscript received September 22, 1938.

tion while others, even though in some instances made in the same open-hearth furnace immediately following or preceding the defective heat, are free of this defect. While it must be presumed that tensional stress is the immediate occasion for shatter cracks such a statement is not illuminating because the internal stress, of thermal origin, may well be of fairly constant magnitude whereas various heats of steel may respond quite differently to such stress. This is brought out by the fact that only a small portion of the steel made develops shatter cracks when cooled in air.

To date two methods are being employed to prevent shatter crack formation, namely Brunorizing and controlled or retarded cooling; the details of both methods are generally well known. A third method which is allied to the controlled cooling process and yet deviates to a marked degree, has been established. The data set forth in this paper outlines this third method. In developing the new method, data secured from the controlled cooling of rail steel supplied information as to the temperature range in which shatter cracks form.

One of the difficulties in any study intended to develop methods of preventing shatter cracks, has been the inability of the investigators to produce a heat of steel when desired which would yield a finished product containing such defects. This remained a serious obstacle until experiments involving the introduction of various gases into liquid ingots showed that by the use of hydrogen a dependable method for producing steel relatively more susceptible to shatter cracks had become available. These experiments indicated that hydrogen incorporated into the steel was apparently a major factor in the development of the cracks formed during cooling.

It is known that the solubility of hydrogen in solid steel decreases with decreasing temperature, a circumstance which tends to force the gas from the cooling metal. It was postulated that if a sufficient time at a suitable temperature were allowed for the major portion of the gas to diffuse from the steel the formation of shatter cracks would be prevented. The delay in cooling to atmospheric temperature evidently prevents the gas and cooling stresses from exceeding the bursting strength of the metal when it is cooled through the destructive shatter crack range, now regarded as being below 400 degrees Fahr.* Confining the study of methods of preventing shatter cracks to the theory postulated, three groups of tests were made, as follows:

*Tests made since this paper was written indicate that shatter cracks form between 100 and 200 degrees Fahr. in shatter sensitive specimens cooled in air without shatter preventive treatment.

1. Controlled or retarded cooling of the steel starting the retardation at different temperatures after the last hot rolling operation.
2. Controlled or retarded cooling of the steel between different temperature ranges after the last hot rolling operation.
3. Regular cooling of the steel to any given temperature between the range of 500 and 1400 degrees Fahr. after the last hot rolling operation and then holding at such temperature for various periods of time, the steel being finally air cooled from the holding temperature.

The first two methods are derivations of the controlled cooling practice now generally used for cooling many steel products to prevent internal defects. The third method is an entirely new process and for certain given holding temperatures from 500 degrees Fahr. up to the critical temperature of the steel eliminates shatter cracks in steel by a schedule which requires a much shorter period of time than the usual controlled cooling process.

All of the tests described in this paper were made on rails since this was a convenient product. Rails rolled from ingots treated with hydrogen were employed, the elimination of shatter cracks in such definitely sensitive rails being a more difficult problem than in regular, untreated rails selected at random, which generally are not susceptible and accordingly often yield entirely negative results.

Methods of Testing

A. Impregnation of the Steel with Hydrogen. Hydrogen was forced into the ingots as the steel was teemed into the ingot mold. A ½-inch double X pipe was used to convey the gas to within 2 inches of the bottom of the ingot mold where the gas was liberated and allowed to bubble through the steel. 30 to 50 pounds per square inch pressure was maintained on the hydrogen line and 15 to 20 cubic feet of gas were fed into each ingot during the period in which it was teemed. The heavy pipe was used in order to prevent it from melting during the gas injection operation.

After the ingots were impregnated with hydrogen they followed the routine channels through the strippers, soaking pits, and rail mill until the finishing end, where the rails received one of the treatments devised to prevent the formation of shatter cracks on cooling to atmospheric temperature. Fig. 1 shows shatter cracks in typical hydrogen-treated rails as regularly cooled in still air. Fig. 2 shows a rail slice cut from an untreated rail of an adjacent ingot of the same

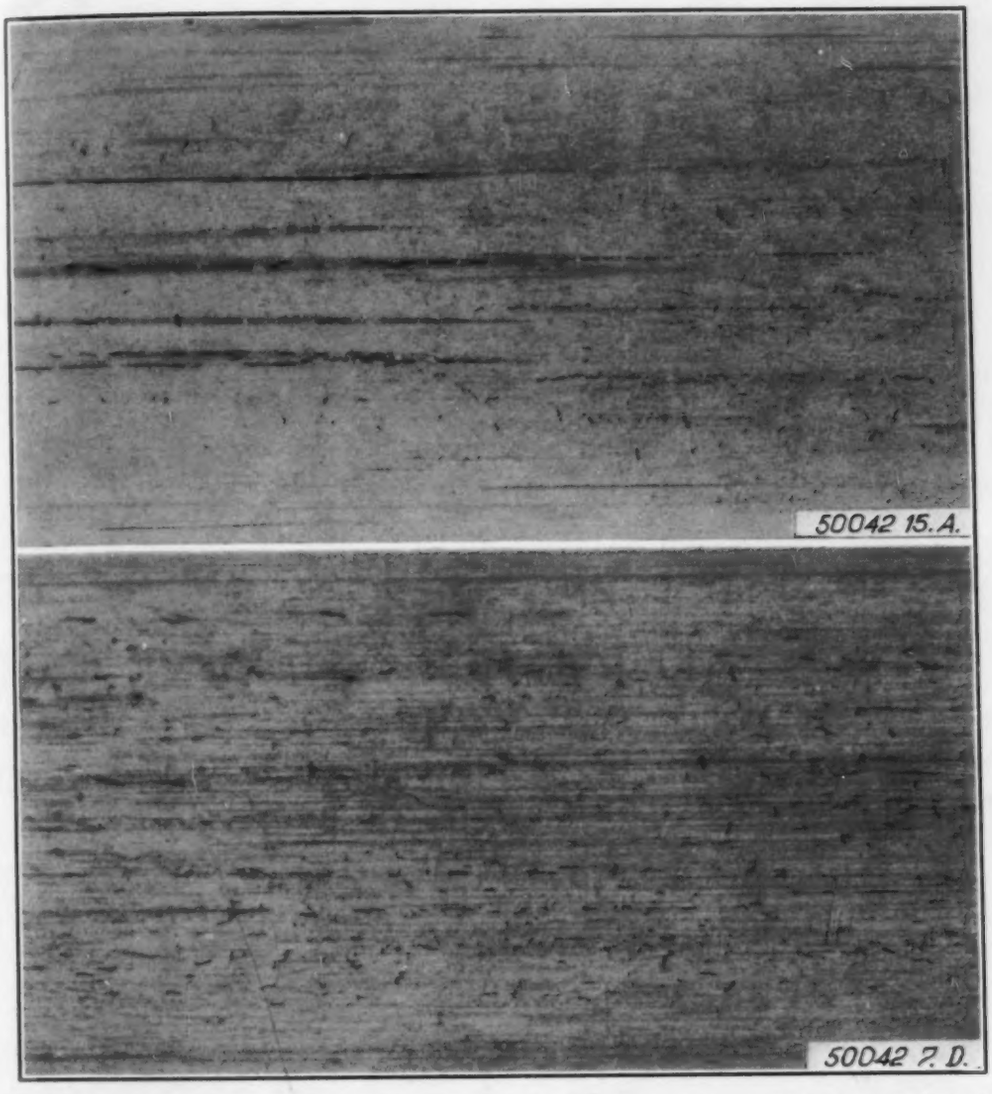


Fig. 1—Hydrogen-Treated Hot Bed Cooled Rail Head Slices Etched in Hot HCl. Heat Number, Ingot Number, and Rail Letter are Shown on Each Slice. Rails Are Badly Shatter Cracked. Approximately ¼ Actual Size.

heat. It is interesting to note the comparative freedom from shatter in this piece as compared to the hydrogen-treated steel. The pieces shown in the figures are horizontal slices cut ⅞ inch below the running surface of the rail head as etched in hot HCl.

B. Controlled or Retarded Cooling of Steel from Different Temperatures After the Last Hot Rolling Operation. Six rails, 2 feet long, were obtained from hydrogen-treated steel at the hot saws. As these rails cooled in air, they were one by one placed in slow-cooling boxes, identical in construction, at different temperatures starting at 800 degrees Fahr. and every hundred degrees thereafter down to 300 degrees Fahr. The rails were held in the boxes

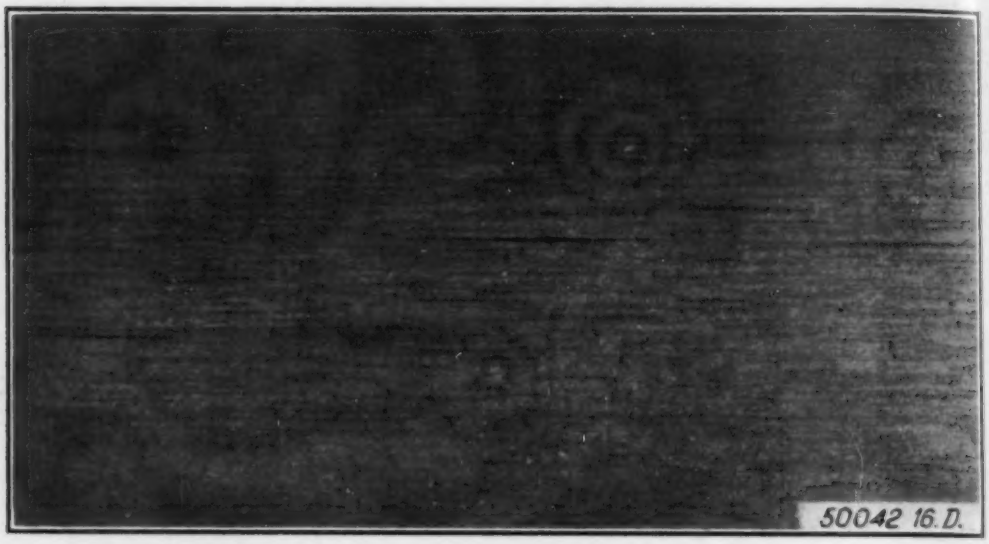


Fig. 2—Hot Bed Cooled Rail Head Slice Obtained from Untreated Steel. Rail from Same Heat as Hydrogen-Treated Rails Shown in Fig. 1. Slice Etched in Hot HCl. Approximately ¾ Actual Size.

until a temperature of 200 degrees Fahr. was reached, after which they were removed, cut, and examined for shatter cracks. Fig. 3 shows the cooling curves for the different rails while Fig. 4 shows the rail head etched slices.

A tabulation of the results is shown in Table II. The chemi-

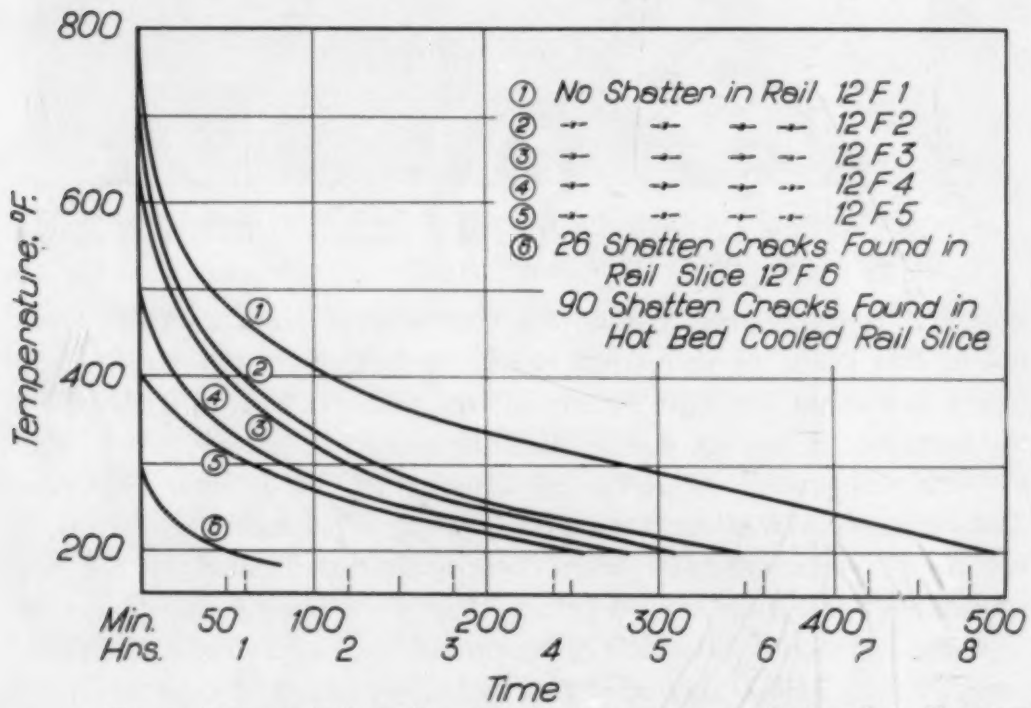


Fig. 3—Study of Rail Cooling Curves to Determine the Cooling Rate Necessary to Prevent Shatter Cracks.

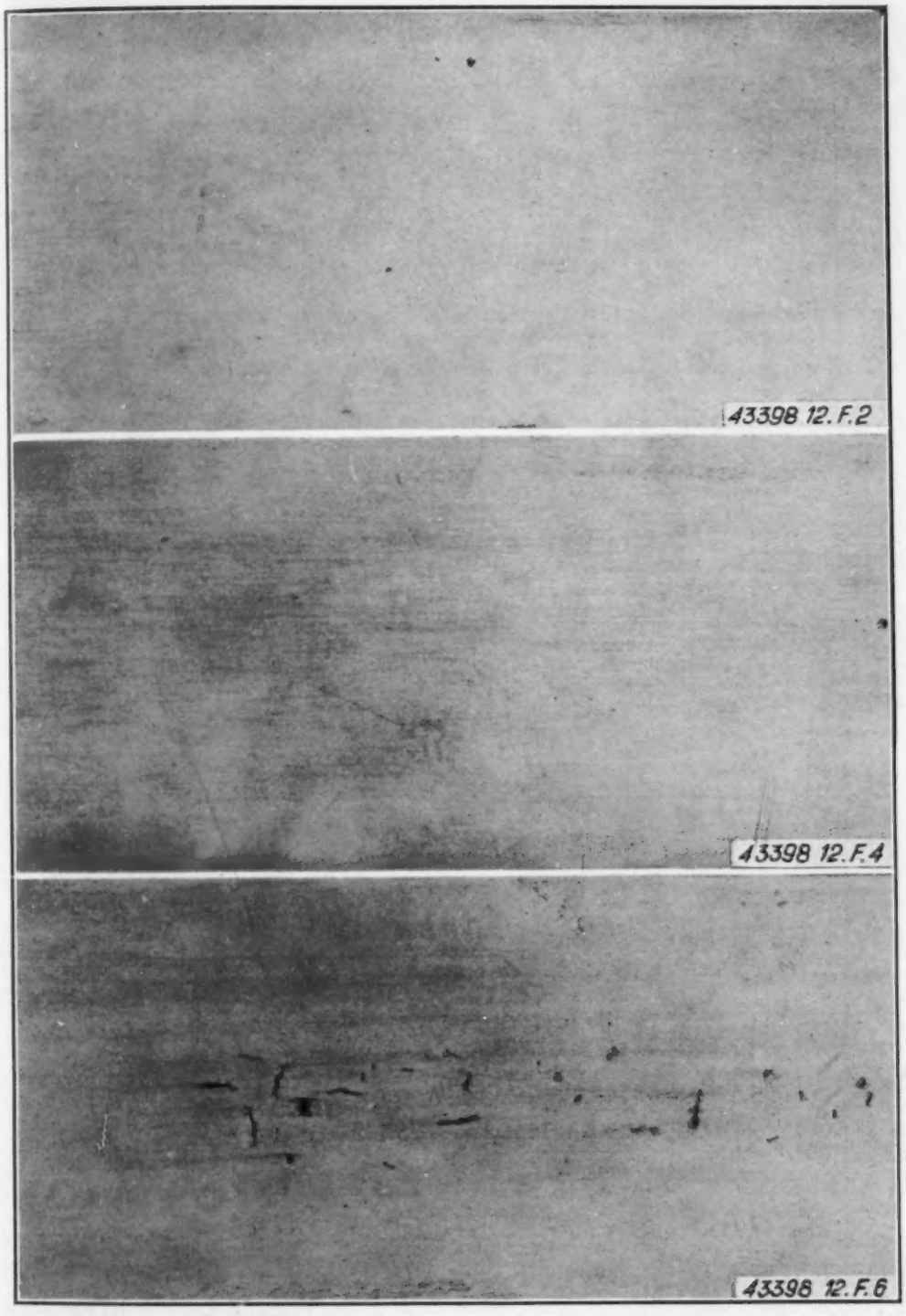


Fig. 4—Rail Head Slices Cut from Hydrogen-Treated Rails Controlled Cooled Between Temperatures Indicated: 12-F-2, 700-200° F.; 12-F-4, 500-200° F.; 12-F-6, 300-200° F. Shatter Cracks Were Found Only in Rail 12-F-6. Slices Were Etched in Hot HCl. Approximately ¾ Actual Size.

cal analyses of all rail heats used in the test are contained in Table I. The results show controlled cooling of rails will prevent the

Table I
Chemical Analyses of Heats Used in Tests

Heat Number	C	Mn	P	S	Si
50042	0.78	0.77	0.024	0.027	0.21
43398	0.72	0.89	0.075	0.026	0.23
35390	0.72	0.84	0.027	0.025	0.23
61093	0.78	0.88	0.015	0.023	0.20
38505	0.77	0.93	0.018	0.026	0.19
48470	0.74	0.85	0.024	0.024	0.20
35390	0.72	0.84	0.027	0.025	0.23
31358	0.78	0.76	0.029	0.028	0.23

Table II
Treatment of Rails and Shatter Crack Tabulation

Test B

Rail	Number	Treatment	Number of Hours of Controlled Cooling	Number of Shatter Cracks Found in 6-Inch Horizontal Rail Head Slice	Temperature Degrees Fahr. of Rail as Placed in Box
43398	12-F-6	Hot Bed Cooled	0	90	
43398	12-F-1	Controlled Cooled	8.25	0	800
43398	12-F-2	Controlled Cooled	5.80	0	700
43398	12-F-3	Controlled Cooled	5.17	0	625
43398	12-F-4	Controlled Cooled	4.70	0	500
43398	12-F-5	Controlled Cooled	4.28	0	400
43398	12-F-6	Controlled Cooled	1.33	26	300

Table III
Treatment of Rails and Shatter Crack Tabulation

Test C

Rail	Number	Treatment	Number of Hours of Controlled Cooling	Number of Shatter Cracks Found in 6 Inch Horizontal Rail Head Slice	Temperature Degrees Fahr. of Rail as Placed in Box	Temperature Degrees Fahr. Rail Removed From Box
35390	8-F-7	Hot Bed Cooled		128		
35390	8-F-1	Controlled Cooled	0.66	100	775	500
35390	8-F-2	Controlled Cooled	1.00	84	775	450
35390	8-F-3	Controlled Cooled	1.41	78	775	400
35390	8-F-4	Controlled Cooled	1.57	77	775	350
35390	8-F-5	Controlled Cooled	2.00	62	725	300
35390	8-F-6	Controlled Cooled	4.83	3	725	250

formation of shatter cracks. The controlled cooling process may start as low as 400 degrees Fahr. with a cooling cycle of 4½ hours between 400 and 200 degrees Fahr. without the occurrence of such defects even in the exceedingly sensitive, hydrogen-treated steel. The cooling cycle necessary to restrict the development of shatter cracks may, in principle, vary to some degree with each rail heat, depending on the shatter sensitivity.

C. Controlled or Retarded Cooling of Steel between Various Temperature Ranges Starting from a Given Temperature After the Last Hot Rolling Operation. Six rails, 2 feet long, hydrogen-treated, were placed in boxes for controlled cooling at approximately 800 degrees Fahr. after cooling in air to this temperature from the last hot rolling operation. The rails were allowed to cool until they

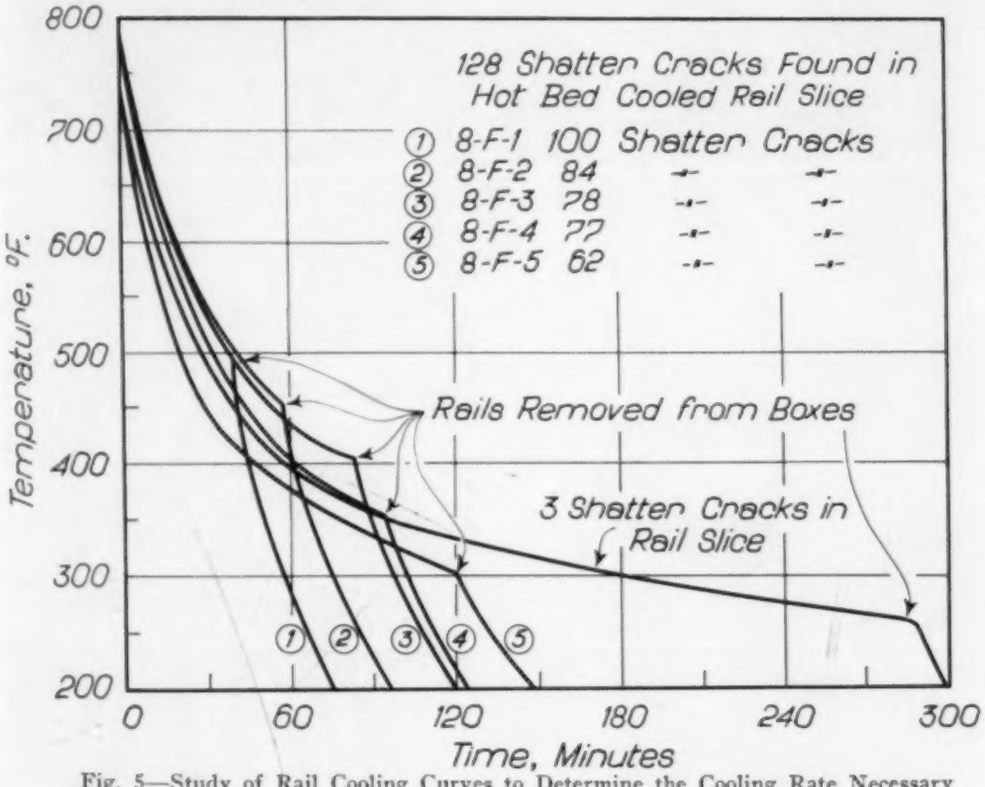


Fig. 5—Study of Rail Cooling Curves to Determine the Cooling Rate Necessary to Prevent Shatter Cracks.

reached 500 degrees Fahr., at which temperature one rail was removed and allowed to cool to atmospheric temperature in still air. The same procedure was repeated at 450 degrees Fahr. and every 50 degrees Fahr. thereafter to 250 degrees Fahr. Figs. 5 and 6 show respectively the cooling curves and the etched slices.

A tabulation of the results is shown in Table III. It is interesting to note that the shatter cracks materially decreased with increased temperature range and longer time of controlled cooling. With this rail heat a cooling cycle of 4.8 hours was not sufficient to entirely eliminate shatter cracks in the steel. The heat was a little more sensitive to shatter cracks than the heat used for tests under section B.

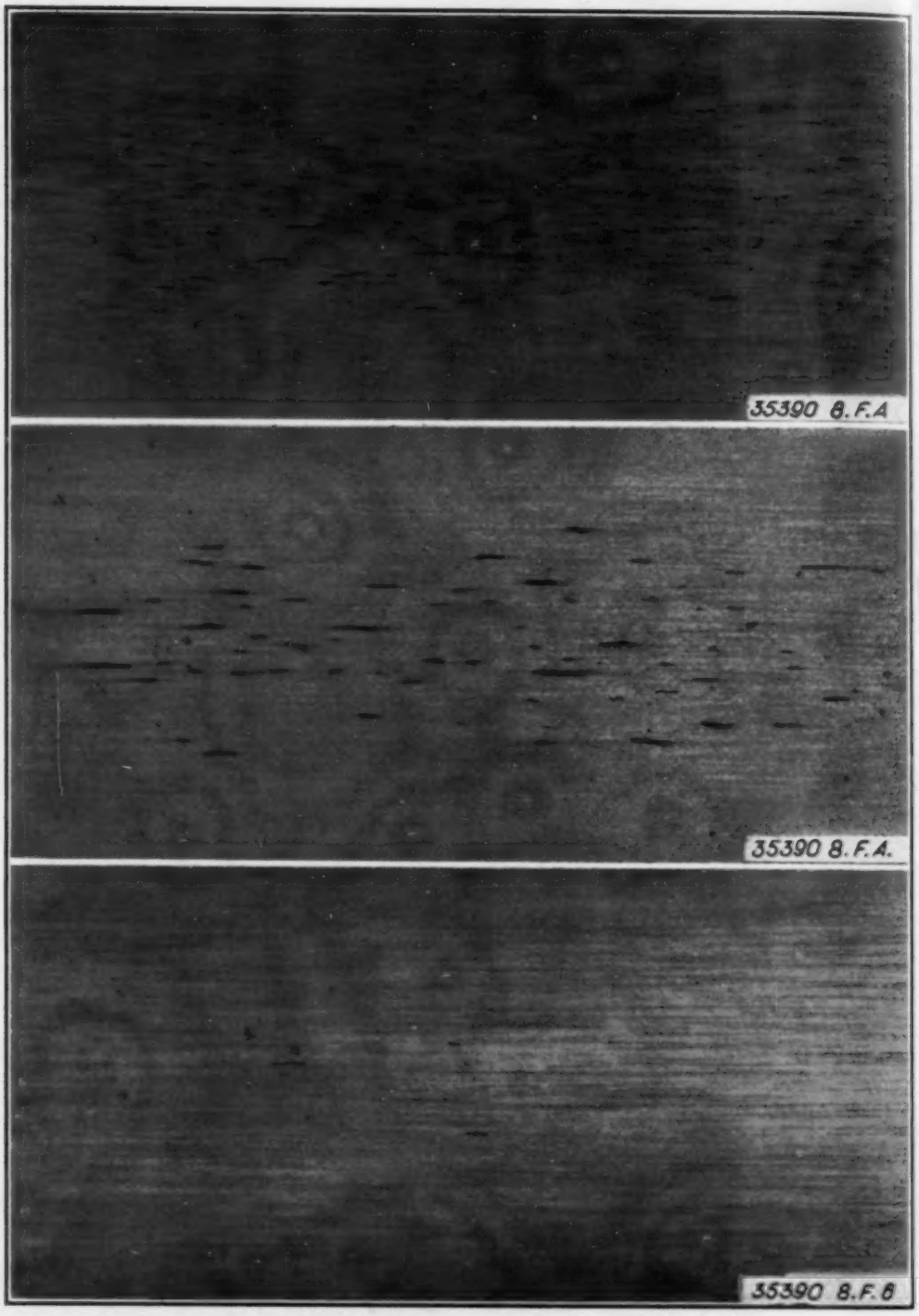


Fig. 6—Rail Head Slices Cut from Hydrogen Treated Rails Controlled Cooled Between Temperatures Indicated: 8-F-2, 775-450° F.; 8-F-4, 775-350° F.; 8-F-6, 725-250° F. Shatter Cracks Can Be Seen in All Slices. Slices Were Etched in Hot HCl. Approximately ¾ Actual Size.

D. Steels Air-Cooled to Any Temperature Within the Range of 500 to 1400 degrees Fahr. After the Last Hot Rolling Operation and Held for Various Periods of Time at This Temperature Followed

by Cooling in Air. Seven to eleven rail specimens, for the series of constant-temperature periods, were obtained for each of the six holding-test temperatures of 500, 600, 800, 1000, 1200, and 1400 degrees Fahr. Each group of specimens was taken from the same ingot and

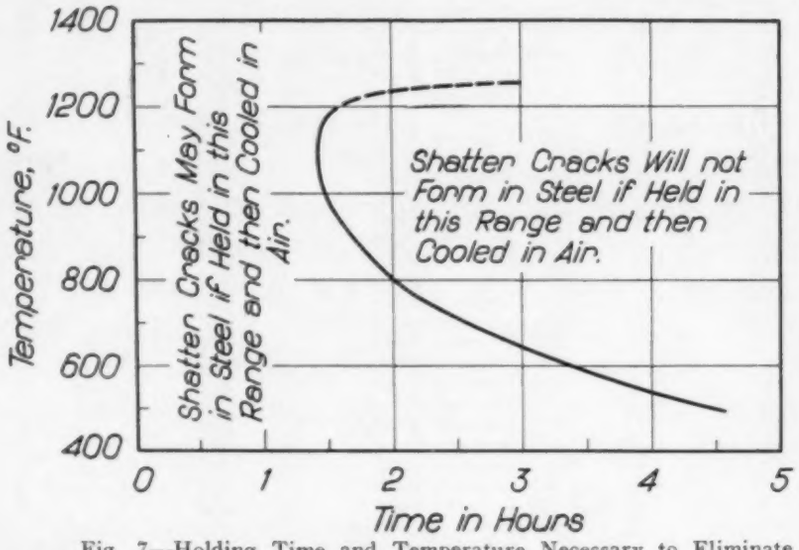


Fig. 7—Holding Time and Temperature Necessary to Eliminate Shatter Sensitivity in 112-Pound Rails.

as far as practical cut from adjacent rails at the hot saws. When the rails had cooled normally to the selected temperature after the last hot rolling operation they were charged into a furnace and held at this temperature. One rail was removed from the furnace after a given period of time and thereafter every 15 or 30 minutes, depending on the cycle used. This procedure was used to determine the minimum time required at a given temperature to eliminate shatter sensitivity in the steel. After the rails were removed from the furnace they were allowed to cool in air. Slices were then cut from the rail heads and were etched for shatter cracks. From a study of Table IV it will be seen that 4½ hours were necessary to eliminate shatter at 500 degrees Fahr. as compared to 1½ hours at 1000 and 1200 degrees Fahr. It is interesting to note from Table IV that holding of rails at 1400 degrees Fahr., a temperature for this type steel, had no effect on shatter crack elimination. These results indicate that holding of the steel at some temperature just under the critical temperature is the most effective, possibly because this temperature range is the optimum for allowing the gases to diffuse from the metal. Fig. 7 shows the results of the tests plotted in graphical form which gives a U-shaped curve. Rails of sensitive steel held at any given temperature between 500

Table IV

Results of Tests for Shatter Cracks in Rails Held in Furnace at Temperatures from 1400 to 500 degrees Fahr. for Various Lengths of Time and Then Air Cooled

Rail	Number	Lab. No.	Temperature of Steel Charged and Held in Furnace	Number of Hours in Furnace	Approximate Number of Shatter Cracks in 6x⅞ Inch Rail Head Slice
61093	8-C-1		1400 Degrees Fahr.	1	61
61093	8-C-2		1400 Degrees Fahr.	1¼	58
61093	8-C-3		1400 Degrees Fahr.	1½	62
61093	8-C-4		1400 Degrees Fahr.	1¾	59
61093	8-D-5		1400 Degrees Fahr.	2	56
61093	8-D-6		1400 Degrees Fahr.	2½	59
61093	8-D-7		1400 Degrees Fahr.	3	65
61093	8-D-8		Hot Bed Cooled Rail		Numerous
61093	6-C-1		1200 Degrees Fahr.	1	33
61093	6-C-2		1200 Degrees Fahr.	1¼	11
61093	6-C-3		1200 Degrees Fahr.	1½	0
61093	6-C-4		1200 Degrees Fahr.	1¾	0
61093	6-D-5		1200 Degrees Fahr.	2	0
61093	6-D-6		1200 Degrees Fahr.	2½	0
61093	6-D-7		1200 Degrees Fahr.	3	0
61093	6-D-8		Hot Bed Cooled Rail		Numerous
38505	12-C	1	1000 Degrees Fahr.	½	8
38505	12-C	2	1000 Degrees Fahr.	¾	1
38505	12-C	3	1000 Degrees Fahr.	1	1
38505	12-C	4	1000 Degrees Fahr.	1¼	1
38505	12-B	5	1000 Degrees Fahr.	1½	0
38505	12-B	6	1000 Degrees Fahr.	1¾	0
38505	12-B	7	1000 Degrees Fahr.	2	0
38505	12-B	8	1000 Degrees Fahr.	2¼	0
38505	12-B	9	1000 Degrees Fahr.	2½	0
38505	12-B		Hot Bed Cooled Rail		Numerous
38505	12-D		Hot Bed Cooled Rail		Numerous
48470	14-B		800 Degrees Fahr.	½	62
48470	14-B		800 Degrees Fahr.	1	16
48470	14-B		800 Degrees Fahr.	1½	5
48470	14-B		800 Degrees Fahr.	2	0
48470	14-B		800 Degrees Fahr.	2½	0
48470	14-B		800 Degrees Fahr.	3	0
48470	14-D		800 Degrees Fahr.	3¼	0
48470	14-D		800 Degrees Fahr.	3½	0
48470	14-D		800 Degrees Fahr.	4	0
48470	14-D		800 Degrees Fahr.	4½	0
48470	14-D		800 Degrees Fahr.	5	0
48470	14-D		Hot Bed Cooled Rail		Numerous
35390	8-E	1	600 Degrees Fahr.	½	77
35390	8-E	2	600 Degrees Fahr.	1	31
35390	8-E	3	600 Degrees Fahr.	1½	35
35390	8-E	4	600 Degrees Fahr.	2	25
35390	8-E	5	600 Degrees Fahr.	2½	18
35390	8-E	6	600 Degrees Fahr.	3	1
35390	8-E	7	600 Degrees Fahr.	3½	0
35390	8-E	8	600 Degrees Fahr.	4	0
35390	8-E	9	600 Degrees Fahr.	4½	0
35390	8-E	10	600 Degrees Fahr.	5	0
35390	8-A		Hot Bed Cooled Rail		Numerous
35390	8-C		Hot Bed Cooled Rail		Numerous
31358	8-D	1-D	500 Degrees Fahr.	½	57
31358	8-D	2-D	500 Degrees Fahr.	1	51
31358	8-D	3-D	500 Degrees Fahr.	1½	63
31358	8-D	4-D	500 Degrees Fahr.	2	31
31358	8-D	5-D	500 Degrees Fahr.	2½	11
31358	8-F	6-D	500 Degrees Fahr.	3	8
31358	8-F	7-D	500 Degrees Fahr.	3½	2
31358	8-B	8-D	500 Degrees Fahr.	4	1
31358	8-B	9-D	500 Degrees Fahr.	4½	0
31358	8-B	10-D	500 Degrees Fahr.	5	0
31358	8-D	17-D	Hot Bed Cooled Rail		Numerous
31358	8-F	18-D	Hot Bed Cooled Rail		Numerous

degrees Fahr. and the critical temperature for a period of time corresponding to a point on the left side of the curve and then cooled in air to atmospheric temperature might still have some tendency to

develop shatter. If the holding time and temperature cycle corresponded to a point on the right side of the curve no shatter cracks would be developed in the rail when cooled in air to atmospheric temperature.

Summary of Results

The three groups of tests have shown that time as well as a definite temperature range, approximately 400 degrees Fahr. on the low side and the critical temperature on the high side, are essential factors in the prevention of shatter cracks in shatter sensitive steel. As all of the tests reported in this paper were made on one rail section the question of mass did not enter the picture. The approximate size of the rail head from which the test slices were cut was 2¾ x 1⅝ inches. From other tests made on 6 and 18-inch diameter rounds it was verified that mass affects the time cycle to a considerable extent.

The three factors, time-temperature-mass, that must be given consideration to prevent shatter formation, seem to be compatible with and lend support to the gas diffusion theory advanced by Cramer[1], Bennek[2] and others. The hypothesis is that during the steel-making process, hydrogen is absorbed by the steel. That such gas is in the steel has been shown by Hare[3], Chipman[4], Motok[5] and others. Recent tests also made by the authors have shown that hydrogen is given off of rail steel as it solidifies. After the steel is teemed and is cooling the hydrogen that was absorbed starts to diffuse due to the lowering of the solubility with decreasing temperature. The effusion is maintained at various rates until a temperature of approximately 400 degrees Fahr. is reached. At this point a change in the effusion rate occurs, as shown by Ham[6], which is thought to cause destructive stresses to be developed if sufficient hydrogen is present. While shatter crack formation is not well understood the above theory appears to have some foundation.

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[1]R. E. Cramer, "The Production of Flakes in Steel by Heating in Hydrogen," Transactions, American Society for Metals, Vol. 25, Sept., 1937.

[2]H. Bennek, H. Schenck, and H. Muller, "The cause of the Occurrence of Flakes in Steel," *Stahl und Eisen*, Vol. 55, 1935, p. 321.

[3]W. Hare, L. Peterson, and G. Soler, "An Improved Method for Determining Gas Content of Molten Steel," Transactions, American Society for Metals, Vol. 25, Sept., 1937.

[4]J. Chipman and A. M. Samarin, "Effect of Temperature upon Interaction of Gases with Liquid Steel," *Metals Technology*, January, 1937.

[5]G. T. Motok, "A New Tool for the Control of Quality Steel Making," Transactions, American Society for Metals, Vol. 25, June, 1937.

[6]W. R. Ham, "The Diffusion of Hydrogen Through Nickel and Iron," Transactions, American Society for Metals, Vol. 25, 1937.

Conclusions

Shatter cracks tend to form below 400 degrees Fahr.* in shatter sensitive steel cooled in air from hot rolling temperatures.

Shatter cracks or flakes can be prevented by controlled cooling of the steel after the last hot rolling operation from any temperature above 400 degrees Fahr. with the proper time cycle. In the case of 112-pound rails, the steel of which was hydrogen-treated, 4½ hours were required in cooling between 400 and 200 degrees Fahr. for a minimum time and temperature to prevent shatter.

After rolling, cooling of steel at a retarded rate over a given temperature range above 400 degrees Fahr. followed by cooling in air will prevent shatter if the length of time of retarded cooling is sufficient.

Steels held at any temperature after the last hot rolling operation within the range of 500 degrees Fahr. and the critical temperature for a sufficient period of time, depending in part on the mass, will not develop shatter cracks on cooling in still or circulated air after removing from the furnace or holding box. For rail steel, holding temperatures around 1000-1200 degrees Fahr. seem to be the most effective in preventing shatter cracking in the steel, although the temperature at which shatter cracks form is below 400 degrees Fahr.

Holding of the just-rolled and still untransformed steel above the critical temperature was not effective in preventing shatter cracks from forming in the metal when subsequently cooled in air to atmospheric temperature.

Acknowledgments

The work reported in this paper has been done in the Metallurgical Division of Gary Works, Carnegie-Illinois Steel Corporation, which division is under the supervision of A. D. Beers. It is wished to acknowledge the co-operation and assistance rendered by E. P. Epler and other members of this division during the making of the tests and in compiling the test data.

*Tests made by the authors after this paper was written indicate that rails can be air cooled as low as 200 degrees Fahr., reheated and controlled cooled or subjected to the time-temperature holding process without the formation of shatter cracks.

MAGNETICALLY SOFT MATERIALS

By T. D. Yensen

Abstract

Several sometimes conflicting characteristics are required in magnetically soft materials, the relative importance of which depends upon the application. It is for this reason that a number of different magnetic alloys ranging from pure iron through the silicon irons to the high nickel-iron alloys have been developed, each of which has characteristics which render it particularly suitable for a specific group of applications.

The characteristics of importance are:

(1) Hysteresis loss on passing through a magnetic cycle and arising from internal magnetic "friction". This should be low.

(2) Eddy current loss—due to electric currents induced in the material by changes in flux. This should be low.

(3) Magnetic permeability—should be high and sometimes must be high or constant at low field strengths.

(4) Saturation value should be as high as other considerations permit.

(5) In special applications a definite change in permeability with temperature is required.

(6) The cost, availability and ease of processing are important.

Effect of Impurities

As the ferromagnetic properties are a function of the regularity of the space lattice, it follows that anything that affects this regularity will also affect the magnetic properties. Impurities like carbon, sulphur, nitrogen and oxygen are particularly harmful, because when in solution they occupy interstitial spaces in the crystal lattice and small amounts therefore produce large effects (1)[1] (p. 70). Furthermore, as the solubility is low at room temperature, the excess amount is slowly precipitated in the form of small particles inside the grains with even greater disturbing effect, usually referred to as

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

The author, T. D. Yensen, is manager, Magnetic Division, Westinghouse Electric and Manufacturing Co., E. Pittsburgh, Pa. Manuscript received February 25, 1939.

"aging" (1) (p. 90). Carbon especially should be kept low in iron and iron-silicon alloys in order to obtain low hysteresis loss and high maximum permeability. The amount should not be over 0.01 per cent and preferably less than 0.005 per cent, Fig. 1. Sulphur and oxygen should likewise be held down to similar values.

Effect of Grain Size

Because of the disturbances at the grain boundaries, the fewer the grain boundaries the better are the magnetic properties, which is

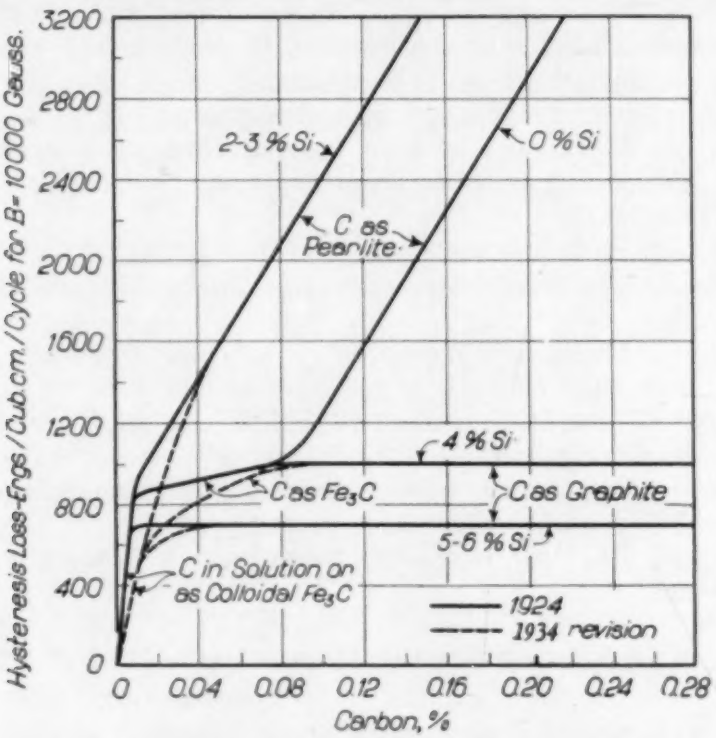


Fig. 1—Effect of Carbon on the Magnetic Properties of Iron-Silicon Alloys.

another way of saying that the grain size should be as large as possible with the single crystal as the limit, Fig. 2.* However, when used on alternating current the eddy loss increases with grain size, so that a compromise should be reached. A grain size of 1 square millimeter seems to be the optimum size in silicon-iron.

Effect of Grain Orientation

Almost all ferromagnetic materials are magnetically anisotropic, i.e., they have different magnetic properties in the different crystal-

*Ref. 1, p. 87. See also Richer: The Iron and Steel Institute, No. II for 1937, p. 323.

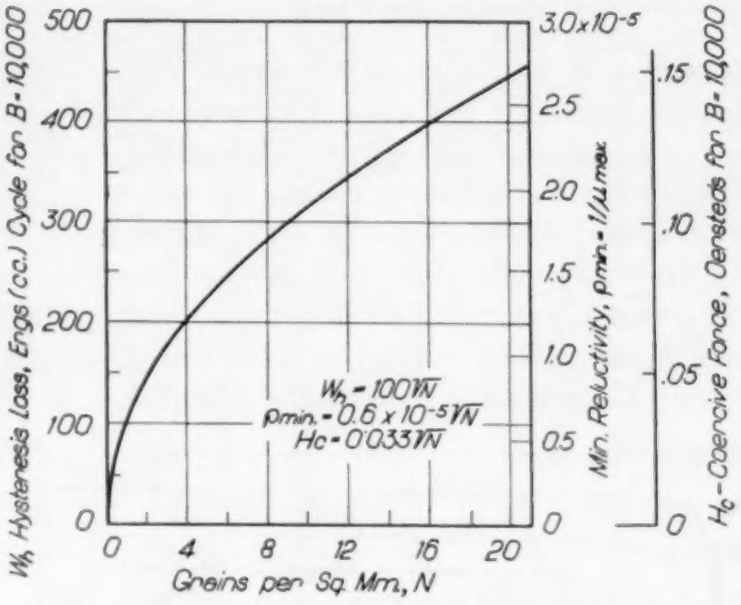


Fig. 2—Net Effect of Grain Size on Magnetic Properties of Pure Iron.

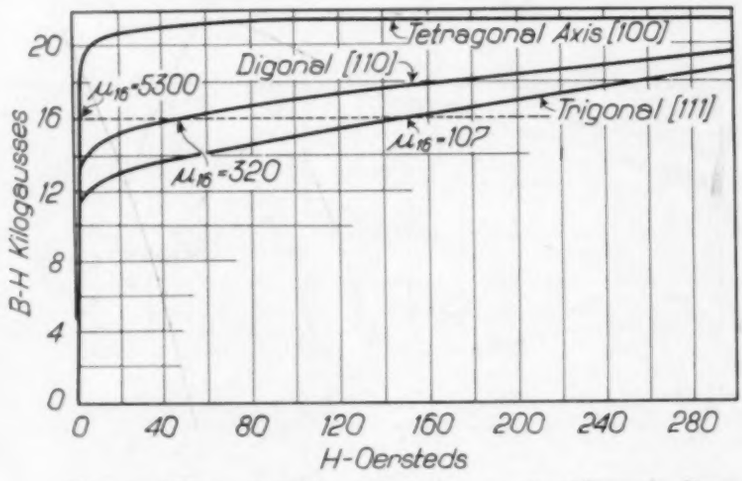


Fig. 3—Effect of Grain Orientation on the Magnetic Properties of Iron.

lographic orientations. This is shown in Fig. 3 for iron (2) and in Fig. 4 for an iron-silicon alloy with 3.85 per cent silicon (3). In both of these cases the direction parallel to a cube edge [100] is the one having the highest permeability. In other cases this is not so, for example in nickel the situation is just the reverse: the direction of easy magnetization is that of the body diagonal [111]. But in all cases we shall have to take the crystal orientation into account in controlling the magnetic properties of ferromagnetic materials.

Effect of Alloying Elements

While pure iron may in many respects be regarded as the ideal ferromagnetic material, it has certain drawbacks that make it unsuitable for practical use especially in alternating current circuits: the resistivity is low, necessitating rolling the iron very thin to keep eddy currents down, and when this is done, the magnetic properties are poor. One of the main objects of alloying elements is therefore to raise the electrical resistivity of iron so as to enable us to use it to advantage in alternating current circuits (which means perhaps 75 per cent of all applications of magnetic materials in industry).

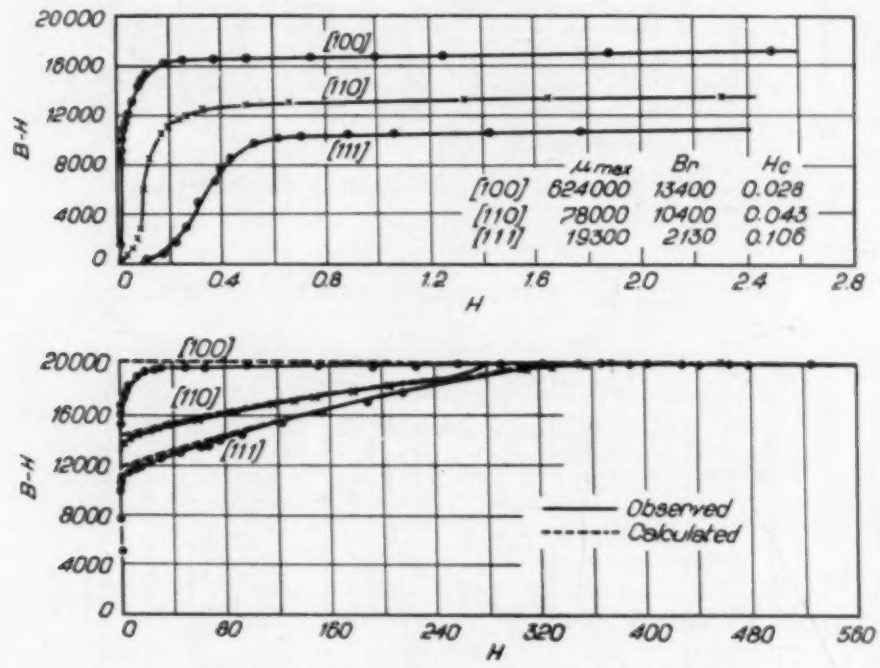


Fig. 4—The Observed and Calculated Magnetization Curves for the (100), (110) and (111) Directions of Single Crystals of 3.85 Per Cent Silicon Iron.

Fig. 5 shows how the various elements affect the resistivity of iron. Outside of carbon in solution, silicon and aluminum increase the resistivity more than any other element.

These two elements also have another important effect: they eliminate the allotropic transformations in iron, so that the alloys can be annealed at high temperatures without recrystallization on cooling, thus enabling us to obtain large grains. Both these elements are substitution elements and for this reason can be added to iron in fairly large quantities without affecting seriously the magnetic properties, although they do reduce the saturation value. However, more

than 4.5 per cent silicon or 8 per cent aluminum makes iron too brittle for most commercial use.

Another reason for keeping the alloying elements down to low values is that outside of cobalt all elements lower the saturation value of iron, Fig. 6. The chief difficulty in connection with silicon

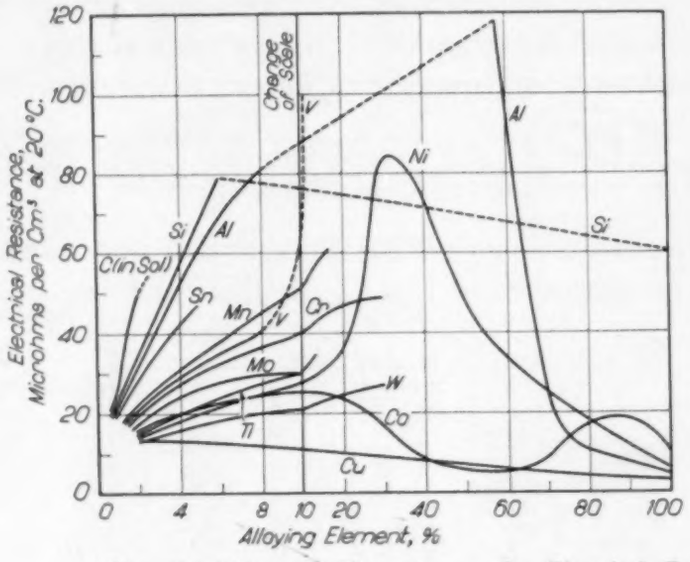


Fig. 5a—Effect of Elements on the Electrical Resistance of Iron.

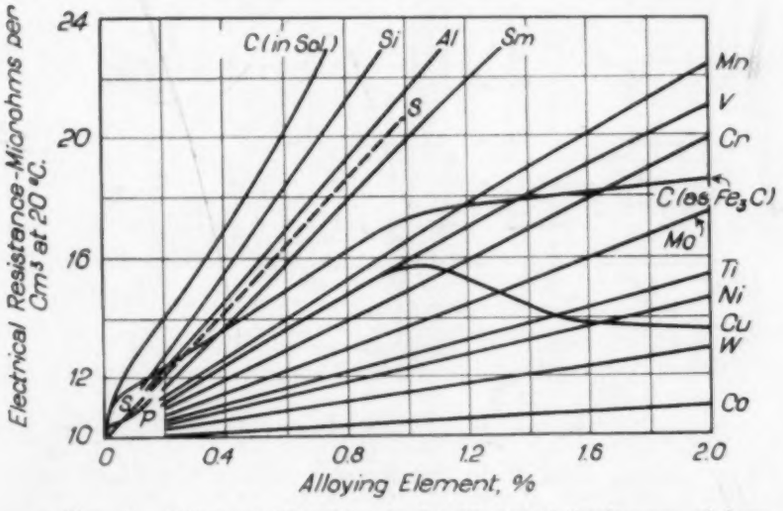


Fig. 5b—Effect of Elements on the Electrical Resistance of Iron.

and aluminum is that they form very stable oxides, so that if the iron is not thoroughly deoxidized before adding the alloying elements, oxide inclusions are formed that cannot again be eliminated and have very deleterious effects on the magnetic properties. Aluminum is particularly bad in this respect.

Unsuspected and valuable magnetic properties are obtained by combining iron with nickel or with nickel and cobalt and by adding to these combinations other elements like copper, molybdenum, or chromium, as will be seen in a later paragraph.

Finally ferromagnetic alloys can be obtained by combining in certain ways several nonferromagnetic elements, as for example Heusler alloys, containing aluminum, manganese and copper. However, as these are not of commercial importance, they will not be considered in this paper.

Magnetic Materials

Iron—Several years ago (1928) the question was asked, "What are the magnetic properties of iron?" At that time data indicated a

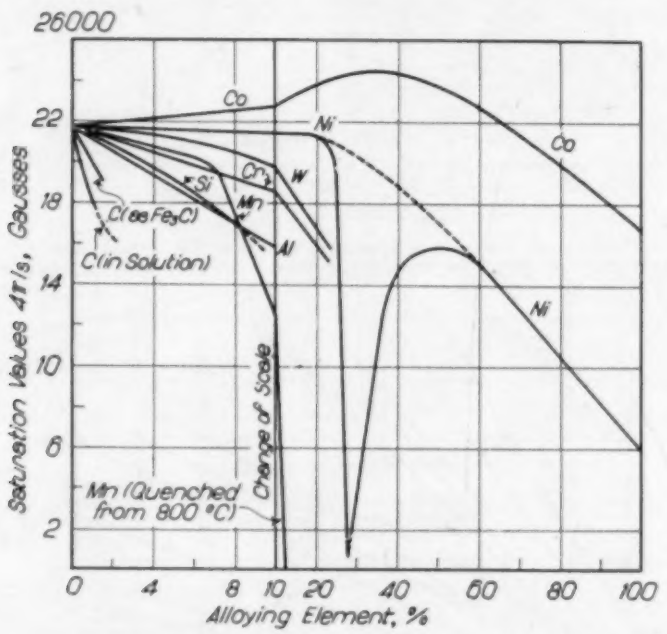


Fig. 6—Effect of Elements on the Saturation Values of Iron.

maximum permeability approaching infinity and a hysteresis loss approaching zero. Since that time the actual values obtained have confirmed this extrapolation. By careful preparation of a single crystal of iron Cioffi has obtained a maximum permeability of 1,430,000 (4) and Mr. Ziegler and the author have prepared ring samples of iron having a hysteresis loss of 70 ergs per cubic centimeter per cycle for B = 10,000 (5).

For experimental uses iron can now be obtained with a purity of 99.95 per cent or even better, having magnetic properties as shown

in Fig. 7: maximum permeability of about 100,000 and a hysteresis loss for B = 10,000 of about 100 ergs per cubic centimeter per cycle.

The latest saturation value of iron comes from the Physikalisch-Technische Reichsanstalt (6) and is given as

$$4\pi I_\infty = 21580 \pm 10 \text{ gauss}$$

based on a density of 7.878.

These values agree well with those given by Cleaves and Thompson (7). The electrical resistivity given by Cleaves and Thompson

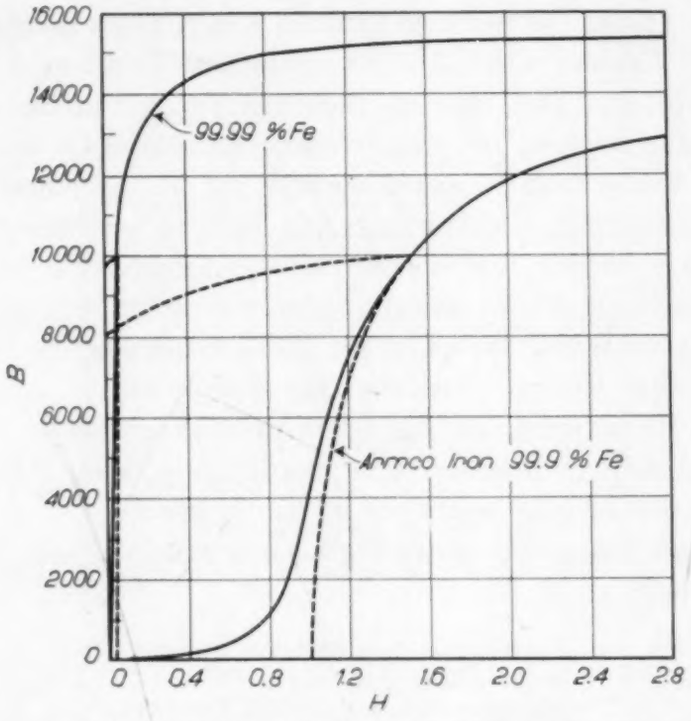


Fig. 7—Hysteresis Loops and B-H Curves for Nearly Pure Iron.

as the most reliable value is 9.8 microhms per cubic centimeter at 20 degrees Cent. with a temperature coefficient of 0.0065 per degree Cent.

Iron-Silicon Alloys—As already stated, pure iron may in many respects be regarded as the ideal magnetic material, but it is easier to obtain good magnetic properties in iron by the use of a small amount of silicon than without it as discovered by Hadfield (8) and shortly afterwards made use of by Gumlich (8). Brittleness imparted by the silicon limits the amount in practice to about 4.5 per cent, although 6 per cent may be used for special purposes.

The commercial grades of silicon iron in common use are made

in basic open-hearth or electrical furnaces, and contain from 0.5 to 4.5 per cent silicon. Sheets are usually hot-rolled from ⅜-inch sheet bars to gages from No. 20 (0.0375 inch) to No. 30 (0.0125 inch). The finished hot-rolled sheets, which may be up to 48 inches wide and of lengths usually in multiples of the widths but not much over 120 inches long, are pickled to remove scale and then given a small amount of cold rolling to insure satisfactory flatness. They are then annealed in stacks at a high temperature, either in electrically or gas heated furnaces and slowly cooled, after which a certain representative portion (about 0.1 per cent) of the sheets from each anneal are sheared into Epstein strips 3 x 50 centimeters and tested for losses and permeability. The lots are then graded on the basis of these results. Table I shows the properties of the various grades used in the U.S.A. tested in accordance with A.S.T.M. Specification A-34.

These properties are for standard Epstein samples cut 50 per cent with and 50 per cent across the rolling direction of annealed sheets and without reannealing to remove shearing strains. If used altogether in the rolling direction the above losses may be 10 per cent lower, and if the sheared punchings are reannealed the losses may be lowered by 10 per cent, so that 0.014-inch Transformer III grade, tested in the rolling direction after reannealing, should have a loss for B = 10,000 of 0.48 watts per pound or less.

The impurities in the above high grade materials after annealing may be as follows:

Carbon less than 0.03 Per Cent
Sulphur less than 0.02 Per Cent
Phosphorus less than 0.02 Per Cent
Manganese less than 0.10 Per Cent

Of these impurities carbon is the most injurious (Fig. 1), and efforts have constantly been made to lower the carbon content, as well as the sulphur content.

The other important factor is grain structure. While grain size in silicon iron is highly important, as far as losses and low density permeability are concerned, the lattice orientation is more important with regard to high density permeability. Iron-silicon alloys are more easily magnetized in the direction of the cube edge, [100], than in any other direction, as shown in Fig. 4, and methods have been developed during the past five years to roll and heat treat iron-silicon alloys so as to obtain most of the grains with a cube edge parallel to the rolling direction (9). By this means a flux density for H = 10

Table I

Magnetic Properties of Standard Electrical Sheet

Grade	Uses	% Si	Sat. Value $4\pi I_s$	Min. Flux Density for H = 10	Max. Losses—Watts per lb. (*) for 60 cycles						Max. Aging factor
					B = 10,000			B = 15,000			
					0.014 29 gage	0.019 26 gage	0.025 24 gage	0.014 29 gage	0.019 26 gage	0.025 24 gage	
Field	Pole pieces, Frames, etc.	0.5	21500	14000	....	....	....	....	....	....	...
Armature	Generators, Small motors	1.0	21000	13500	1.30	1.55	2.05	3.05	3.65	4.80	...
Electric I	Generators, Small motors	1.0	21000	13500	1.15	1.35	1.75	2.75	3.15	4.10	5%
Electric II	Generators, Induction motors	2.5–3.0	20500	13400	1.00	1.15	1.30	2.35	2.75	3.05	3%
Transformer I	Generators and low frequency transformers	3.0–3.5	20200	13200	0.80	0.95	1.10	1.90	2.25	2.60	2%
Transformer II	60 Cycle transformers	3.5–4.0	19800	13000	0.70	0.85	0.95	1.50	2.00	2.25	nil
Transformer III	High grade distribution transformers	4.0–4.5	19500	13000	0.60	0.75	0.85	1.40	1.76	2.00	nil

(*) To obtain watts per kg multiply by 2.2

of the order of 20 per cent higher than for hot-rolled sheet is obtainable.

By a combination of the above rolling process with a refining annealing process, it is possible to obtain improved magnetic properties when the material is magnetized in the direction of rolling. Although the hysteresis loss in the direction of rolling may be greatly reduced, the total core loss is not so much affected because of the relatively high eddy current losses in laminii of commercial thickness (10).

High grade transformer sheet does not age as-received from the makers (See Table I), i.e., the losses do not increase with time at operating temperatures. But this does not mean that silicon iron is inherently nonaging. Unless the steel manufacturer follows the proper melting and heat treating practice, silicon iron may age considerably under operating conditions.

Fe-Al and Fe-Al-Si Alloys—While aluminum is known to have about the same effect on iron as silicon, both as to electrical resistivity and magnetic properties (11), aluminum has never become a serious competitor on account of the difficulties in connection with the manufacturing processes. However, ternary alloys of iron, silicon and aluminum have recently been investigated by Masumoto (12), who discovered a combination having very interesting properties. This alloy, containing 8-11 per cent silicon and 5-6.5 per cent aluminum, is called "sendust" and is reported to have an initial permeability up to 35,000, a maximum permeability up to 162,000 and a hysteresis loss down to 28 ergs for B = 5,000. With such high silicon and aluminum contents the saturation value is necessarily low ($4 \pi I_{sat} = 11{,}000$) and the alloys must be very brittle.

Sendust has been suggested for loading coils, but it would have to meet severe hysteresis and permeability requirements in compressed core form to offer advantages over the powdered permalloy now used in the U. S. A.

Iron-Nickel Alloys[2]—The latent possibilities of these alloys in the way of high permeabilities for low flux densities were indicated as early as 1910 (13). On the basis of these results development work was started to utilize these possibilities commercially. In 1915 a patent application was filed by the Westinghouse Electric and Manufacturing Company on the use of nickel alloys in current

[2]In the preparation of this section liberal use has been made of Data Sheet No. 2, "Iron Nickel Alloys for Magnetic Purposes" prepared by Mr. J. W. Sands, of The International Nickel Co., Inc., for their Iron Nickel Data Book (1938).

transformers (14), in which a high permeability at low flux densities and low losses are most important. Then followed a systematic investigation of the iron-nickel alloys at the Westinghouse Research Laboratories, the results (15), in general, confirming those of the earlier investigations. The average effect of nickel on the permeability of these alloys after the ordinary heat treatment (annealing and slow cooling) is shown in Fig. 8, showing no particular

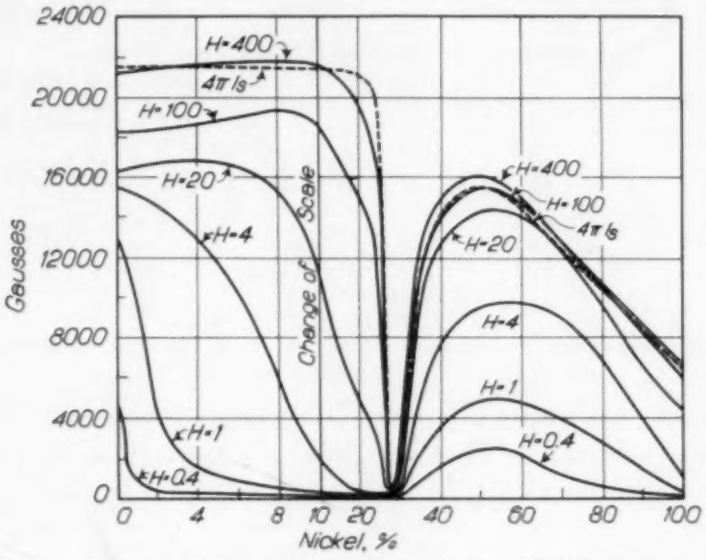


Fig. 8—Magnetic Properties of Iron-Nickel Alloys. Electrolytic Iron and Nickel, Melted and Annealed in Vacuum.

advantage over the best grades of iron and iron-silicon alloys, although individual alloys were obtained in the region of 50 per cent nickel that had unusually good magnetic properties. This led to an intensive study of the 50 per cent alloy as the most promising composition for applications in the power and radio fields. (See later under Hipernik). At the same time the Bell Telephone Laboratories had been working on improved alloys for use in connection with telephone cables, for which purpose the alloys in the region of 70-80 per cent nickel appeared to be the most promising. (See below under Permalloy). By 1923 and 1924 the developments were sufficiently advanced to justify the publication of the preliminary results (16), (17), which in turn have led to the placing on the market of a large number of iron-nickel alloys by various manufacturers, both here and abroad. While these alloys are basically iron-nickel alloys, appreciable percentages of other elements are added in many cases to develop or accentuate some particular characteristic which is desirable for the application in view.

Table II
Commercial Magnetic Iron-Nickel Base Alloys

Name	Per Cent Nickel	Sponsor
Alloys with Very High Permeability at Low Field Strengths		
Permalloy	60-90 + special heat treatment and sometimes + Cr or Mo...	Western Electric Co.
Mumetal	Approx. 76 + 6% Cu and 1.5% Cr	Telcon* and Allegheny-Ludlum Steel Co.
Permafy	Approx. 80	Acieries de Firminy
1040 Alloy	72 + 14% Cu and 3% Mo	Siemens & Halske
High Permeability Alloys for Higher Field Strengths		
45 Permalloy	45	Western Electric Co.
Megaperm 6510	65 + 10% Mn	Germany
Hipernik	50	Westinghouse E. & M. Co.
Hyperm	50	Krupp
Nicaloi	49	General Electric Co.
Audiolloy	48	Crucible Steel Co.
Permenorm	48	Heraeus-Vacuumschmelze
Allegheny Electric Metal.	47	Allegheny-Ludlum Steel Co.
Anhyster C and D	45-50	Acieries d'Imphy
Radiometal	45-50	Telcon*
2129	45-50	Telcon*
Megaperm 4510	45 + 10% Mn	Germany
Moderately High Permeability Alloys of High Electrical Resistance		
Rhometal	40-45 + 5% Cr and 3% Si	Telcon*
Gamma	Approx. 35	Acieries d'Imphy
Anhyster A and B	Approx. 35	Acieries d'Imphy
Alloys with Constant Permeability Over a Range of Flux Densities		
Perminvar	20-75 + 5-40% Co + special heat treatment and sometimes + Mo.	Western Electric Co.
Conpernik	50 + special heat treatment	Westinghouse E. & M. Co.
Isoperm	40-55 + special treatment	Germany
Isoperm (precipitation types)	36-50 + 9-15% Cu	Germany
	40-60 + 3-4% Al	Germany
Alloys with Permeability Varying with Temperature		
Temperature Compensator Alloy	30	Carpenter Steel Co.
Thermoperm	30	Krupp
N. M. H. G.	30	Acieries d'Imphy

*Telegraph Construction & Maintenance Co., Ltd., London, England.

The trade names, approximate composition and applications of the most important iron-nickel alloys are summarized in Table II.

Permalloy—About 20 years ago research at Bell Telephone Laboratories turned to the behavior of iron-nickel alloys at the very low flux densities encountered in telephone apparatus and focused attention on their initial permeabilities. It was found that all annealed alloys containing between 30 and 90 per cent nickel have initial permeabilities higher than that of Armco iron. Alloys containing more than 50 per cent nickel were found to be sensitive to heat treatment as shown in Fig. 9, the particular heat treatment that resulted in improved initial (and also maximum) permeability consisting in air quenching thin strips on a copper block from the magnetic transformation point. The most startling results were ob-

tained for alloys in the neighborhood of 80 per cent nickel (the best composition being 78.5 per cent), and the name "Permalloy" was given to the alloys in this range (16).

Maximum permeabilities of 100,000 are readily obtained with this alloy (see Fig. 10) but the saturation value is low (11,000) and its electrical resistivity is only about double that of iron. How-

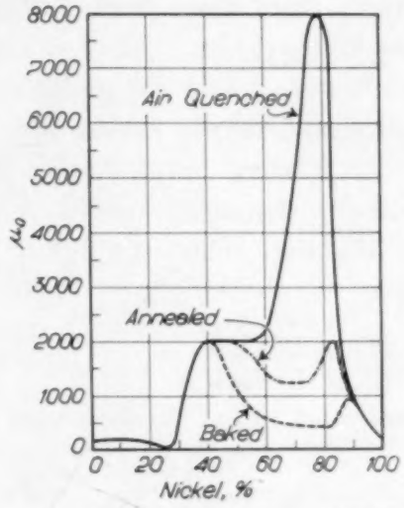


Fig. 9—Initial Permeabilities for the Fe-Ni Series.

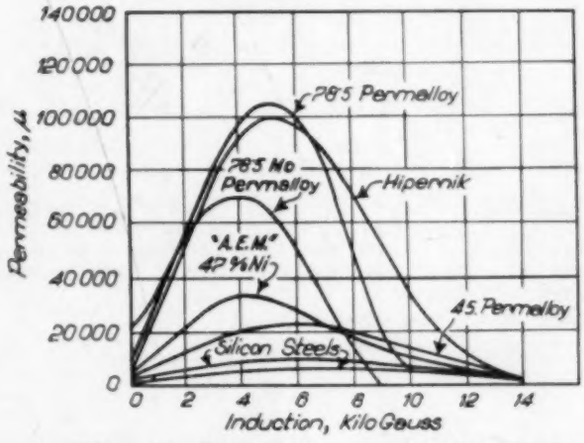


Fig. 10—Permeability Curves for Various Magnetic Alloys.

ever, it was later found that this can be remedied by the addition of chromium or molybdenum, which at the same time eliminates the necessity for air quenching and increases the initial permeability to over 20,000, but at a further sacrifice of saturation value (18). The Bell Telephone Laboratories gradually applied the name Permalloy to all iron-nickel alloys above 30 per cent nickel, the designation being by per cent composition. Thus, "3.8-78.5 Cr

Permalloy" is an alloy of 3.8 per cent chromium + 78.5 per cent nickel. Table III, from a paper by Elmen (19) gives the principal characteristics of the most important Permalloys, together with Armco iron, 4 per cent silicon iron and some Perminvars, which will be discussed in a later paragraph.

The high initial permeability and low hysteresis loss of the 78.5 per cent Permalloys make them very successful as material for continuous loading of submarine cables (20) for the purpose of speeding up the transmission of signals through telegraph cables, and making it possible to use submarine cables for the transmission of speech. The method of loading consists in winding a 0.005-inch thick tape spirally onto the insulated single conductor, annealing it after it has been put on, and then completing the cable with the outer protecting layers.

Table III

Magnetic Properties of Various Permalloys and Perminvars

Material (1)	Initial Permeability	Maximum Permeability	Hysteresis Loss, ergs per cc per cycle (2)	Residual Induction, gausses	Coercive Force, oersteds	Saturation Value, gausses (3)	Resistivity, microhm cm
Armco Iron	250	7,000	5,000	13,000	1.0	22,000	11
4% Silicon-Iron	600	6,000	3,500	12,000	0.5	20,000	50
78.5 Permalloy, quenched	10,000	105,000	200	6,000	0.05	10,700	16
45 Permalloy	2,700	23,000	1,200	8,000	0.3	16,000	45
3.8-78.5 Cr-Permalloy	12,000	62,000	200	4,500	0.05	8,000	65
3.8-78.5 Mo-Permalloy	20,000	75,000	200	5,000	0.05	8,500	55
45-25 Perminvar, baked	400	2,000	2,500	3,000	1.2	15,500	19
7-45-25 Mo-Perminvar, baked	550	3,700	2,600	4,300	0.65	10,300	80
70-7.5 Perminvar, annealed	750	3,500	.....	.....	0.8	12,000	16

(1) Single numbers preceding the word "Permalloy" signify the nickel content, and double numbers signify first the content of chromium or molybdenum, and second the nickel content, the balance being iron in each case. The two large numbers before "Perminvar" indicate the nickel and cobalt contents, respectively, and the small initial number indicates the molybdenum content.

(2) For saturation value of the flux density.

(3) Saturation value of the intrinsic induction.

An even larger application of permalloy is in the loading coils for land telephone cables. At intervals of about a mile the cable, containing as many as 1200 pairs of conductors, enters an iron box in which each pair of conductors is connected in series with a loading coil. In order to use up as little energy as possible in eddy currents and also to get a linear relationship between the current and the flux, permalloy for loading coils is generally used in the form of a powder, which is first insulated, then compressed into doughnut shaped cores and finally annealed (21).

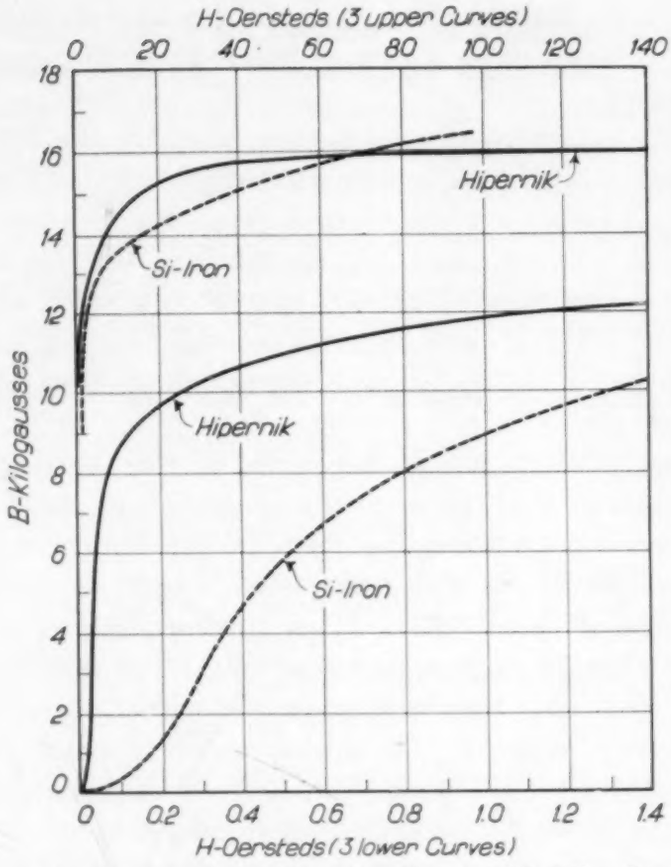


Fig. 11—B-H Curves for Hipernik and High Silicon-Iron.

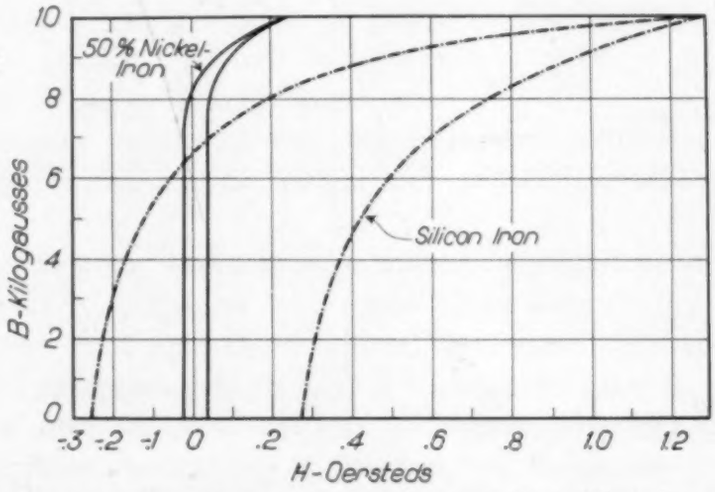


Fig. 12—Hysteresis Loops for Hipernik and High Silicon Iron.

In addition to the above applications the high nickel content permalloys are valuable whenever high initial permeabilities and low losses are of importance, such as for telephone relays, telephone

instruments, radio transformers, etc., but due to their high cost, the lower nickel content alloys (such as hipernik or 45 permalloy) are usually preferred.

Hipernik—As ordinarily made, the alloys in the region of 50 per cent nickel exhibit nothing remarkable (See Fig. 8) except that their saturation values are the highest of all Fe-Ni alloys above 30 per cent nickel. By ordinary pot annealing in electric furnaces, a maximum permeability of 20-25,000 can be obtained with an initial permeability of 2700, if pure material is used. Such an alloy is "45 permalloy" listed in Table III, the permeability curve of which is shown in Fig. 10.

In the early 1920's it was discovered at the Westinghouse Research Laboratories that the magnetic properties of these alloys can be vastly improved by annealing them in dry hydrogen at a temperature of 1000 to 1200 degrees Cent. (1830 to 2190 degrees Fahr.) for several hours (22). This treatment eliminates carbon, sulphur and other impurities, but particularly oxygen. In its improved form this alloy has been given the name "hipernik" (from high permeability nickel). The nickel content is not particularly critical, it may be varied from 40 to 60 per cent, but for highest saturation value it should be kept close to 50 per cent.

Hipernik possesses a much higher permeability and smaller hysteresis loop than ordinary 4 per cent silicon-iron (see Figs. 10, 11 and 12). Although saturating at slightly above 16,000, the permeability of hipernik is higher than that of ordinary silicon-iron even at B = 15,000. As commercially made today in ton lots of 0.014- and 0.005-inch thicknesses, the maximum permeability of hipernik is about 100,000, but higher values are frequently encountered.

The use of hipernik in place of ordinary 4 per cent silicon iron for transformer cores would result in a reduction of energy losses to about one-half. However, because of its high cost, its use is limited to special transformers, such as current transformers, in which, because of its high permeability and low loss, the ratio errors and phase angle deviations are reduced to negligible quantities. Cold-rolled in the form of continuous ribbon, hipernik is particularly suitable for bushing type of current transformers, as in this way there is no waste of material.

While hipernik cannot compete with the high nickel alloys for applications requiring the highest initial permeability, it is prefer-

able for most other uses, because of its higher saturation value, (Fig. 8), high electrical resistivity and lower cost.

In Table IV are listed the magnetic properties of hipernik in comparison with values for Wemco Research Iron, ordinary 4 per cent silicon iron, 45 permalloy and Allegheny electric metal.

Table IV
Magnetic Properties of Hipernik, Allegheny Electric Metal and 45 Permalloy
(In accordance with information obtained from the manufacturers.)

Material	Initial Permeability	Maximum Permeability	Hysteresis Loss, ergs per cc per cycle (1)	Residual Induction, gausses (1)	Coercive Force, oersteds (1)	Saturation Value, gausses	Resistivity Microhm-cm	Form of Sample	Specific Gravity
Wemco Iron (99.95% Fe)	.....	100,000	150	9,000	0.05	21,600	10	Solid ring	7.9
4-4.5% Silicon Iron	500	12,000	800	6,000	0.3	19,500	55	0.014" sheet	7.6
Hipernik	4,500	100,000	100	8,000	0.03	16,000	45	0.014" sheet	8.3
45 Permalloy	2,700	23,000	1,200(2)	8,000(2)	0.3(2)	16,000	45	....	...
Allegheny Electric Metal	5,000	32,500	718	5,500	0.1	16,000	45	....	8.3

(1) For B = 10,000 except as noted.
(2) For B = 16,000.

Table V
Magnetic Properties of Some Foreign Magnetic Alloys

(1) Material	Initial Permeability	Maximum Permeability	Hysteresis Loss, ergs per cc per cycle (B = 5,000)	Coercive Force, oersteds (B = 5,000)	Saturation value, gausses	Resistivity, microhm-cm	Specific gravity
Mumetal	10–30,000	60–100,000	40–60	0.03	6–9,000	42	8.6
Radiometal	2,000	10– 15,000	350	0.4–0.5	15,600	55	8.3
Anhyster B	1,300	.....	...	....	9,000	70	...
Anhyster C	1,500	.....	...	....	13,000	59	...
Anhyster D	2,200	25,000	330	....	15,000	46	...
1040 Alloy	Up to 50,000	100,000	50	....	6,000	56	...
Permenorm 4801 (2)	2,700	19,000	...	0.20	14,000	58	...
Megaperm 6510	4,800	26,000	...	0.08	8,500	58	...
Rhometal	850	5,000	420	....	4,500	..	...

(1) See Table II for chemical compositions.
(2) Constant permeability of over 2,000 for H < 0.06.

Miscellaneous--Numerous modifications have been made in these alloys by the addition of other elements and by variation in the heat treatments. They are made by various companies here and abroad, the most important of which are listed in Table V.[3]

[3]Prepared by Mr. J. W. Sands from data obtained from Acieries d'Imphy, Telegraph Construction and Maintenance Company, and the present author.

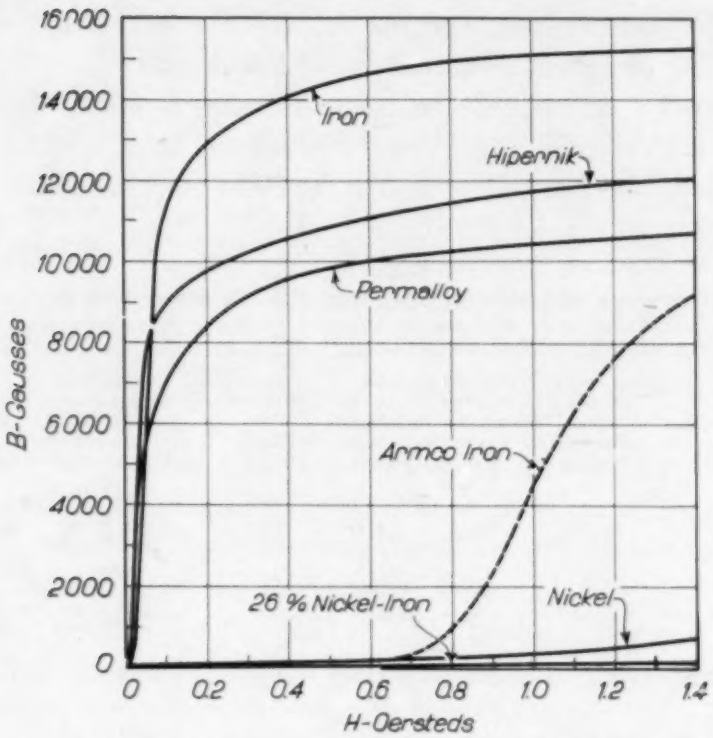


Fig. 13—B-H Curves for the Four Iron-Nickel Alloys 26% Ni, 50% Ni (Hipernik), 78½% Ni (Permalloy) and Nickel with 99.95% Fe and Armco Iron for Comparison.

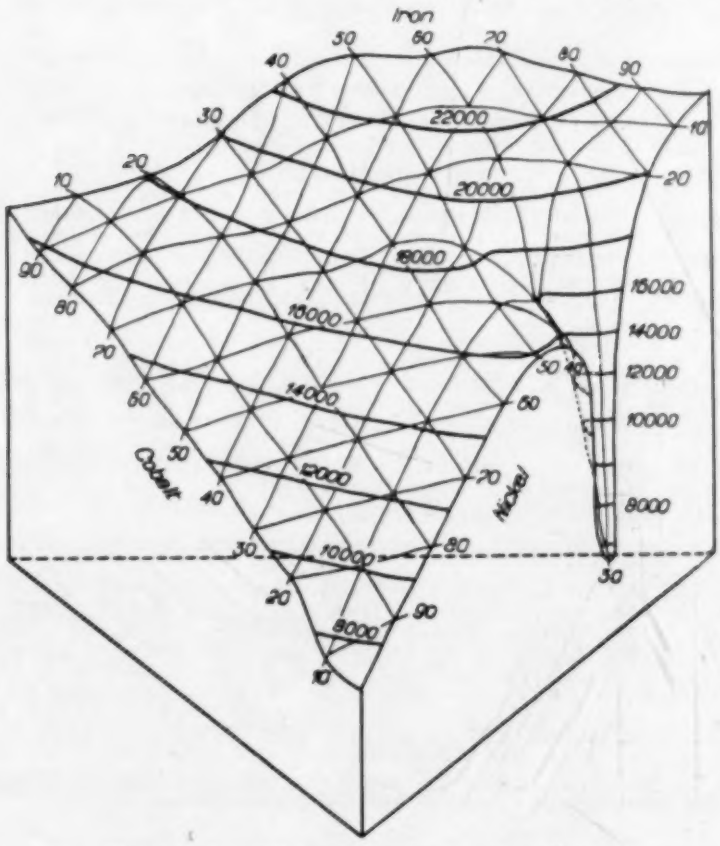


Fig. 14—Iron-Nickel-Cobalt Saturation Values.

By cooling some of these alloys in a magnetic field through the magnetic transformation point, great improvements have been obtained at the Bell Laboratories (23). Particularly good results were obtained with 65 per cent nickel and with 45 per cent nickel, 30 per cent iron, 25 per cent cobalt (perminvar composition). A maximum permeability of over 600,000 was reported for the 65 per cent nickel alloy. The cause of the improvement is explained on the basis of elimination of strains due to magnetostriction.

In Fig. 13 have been plotted for comparison B-H curves for iron, 26 per cent nickel, hipernik, permalloy and nickel.

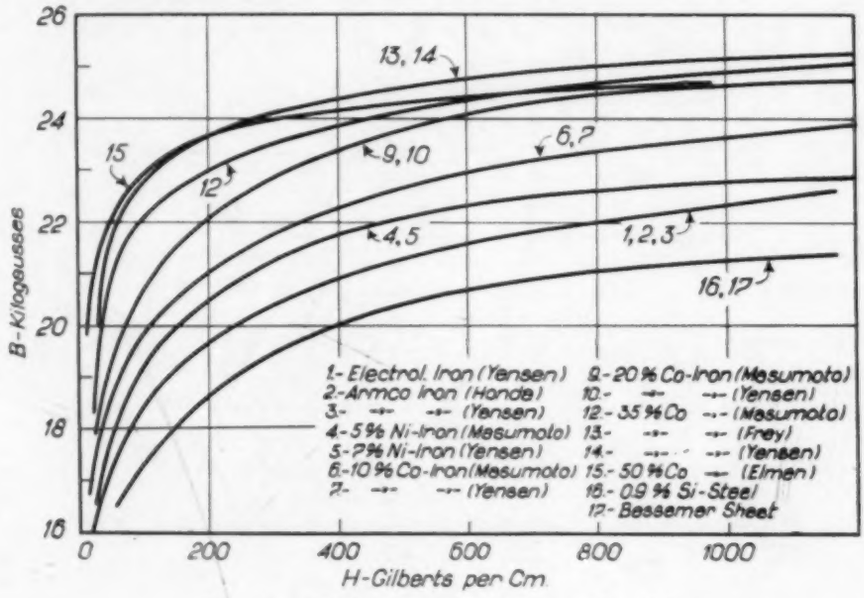


Fig. 15—High Saturation Value Materials.

Materials with High Magnetic Saturation Value—Iron has a saturation value of 21,600 ($4\pi I_s$) (24). In order to exceed this value it is necessary, as far as our present knowledge goes, to alloy iron with cobalt in amounts between 0 and 65 per cent. The highest value is obtained by using 34.5 per cent cobalt. This was discovered by P. Weiss (25) in 1912, who obtained a 10 per cent increase in saturation value, and it was confirmed in 1915 by the author (26), who got a 13 per cent increase. The entire series of Fe-Co-Ni alloys has since been thoroughly investigated by Elmen (27) Fig. 14, and F. Stäblein (28) has collected curves for a number of iron alloys, as shown, slightly modified, in Fig. 6. The value 24,200 may thus be regarded as well established for 34.5 per cent cobalt-iron, corresponding to Fe_2Co. In Fig. 15 have been plotted

B-H curves for a number of materials that are useful where high flux densities are desired.

Curve No. 15 in Fig. 15 is for a 50 per cent cobalt alloy according to Elmen (29). The addition of a small amount of vanadium makes this alloy easy to forge and roll (30), and because of its better magnetic properties below H = 200, it is preferable to the 34.5 per cent alloy where cost is of no importance. The name "permendur" has been applied to this alloy.

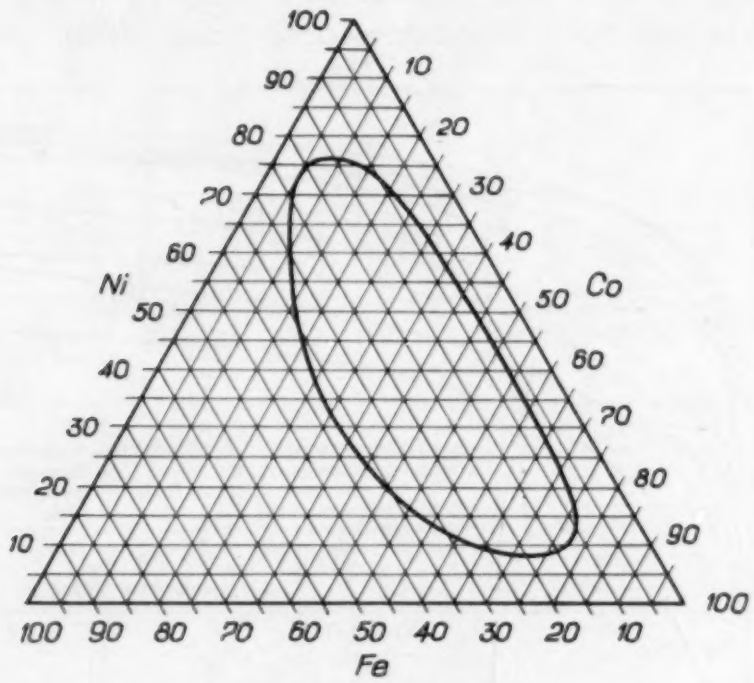


Fig. 16—Perminvar Range.

Materials with Constant Permeability—At the Bell Laboratories were developed certain iron-nickel-cobalt alloys (31) having a constant permeability at low magnetizing forces. These, containing in the neighborhood of 30 per cent iron, 45 per cent nickel, and 25 per cent cobalt, were called "perminvar." They are useful wherever a constant inductance or reactance is essential such as in filter coils for radio circuits or for loading coils for telephone circuits, where air gaps are otherwise used with sheet materials or where iron or permalloy is used in the form of compressed powders. Fig. 16 shows the perminvar range according to Elmen, and Fig. 17 shows the hysteresis loops for the optimum composition. Similar (but not as good) results may be obtained with 50 per cent iron-nickel alloys by means of a special heat treatment which, in fact,

is an incomplete annealing below 800 degrees Cent. (1470 degrees Fahr.). Such an alloy, developed independently at the Bell Laboratories and at the Westinghouse Research Laboratories, has by the latter been called "conpernik" to distinguish it from "hipernik," as both have essentially the same composition (32).

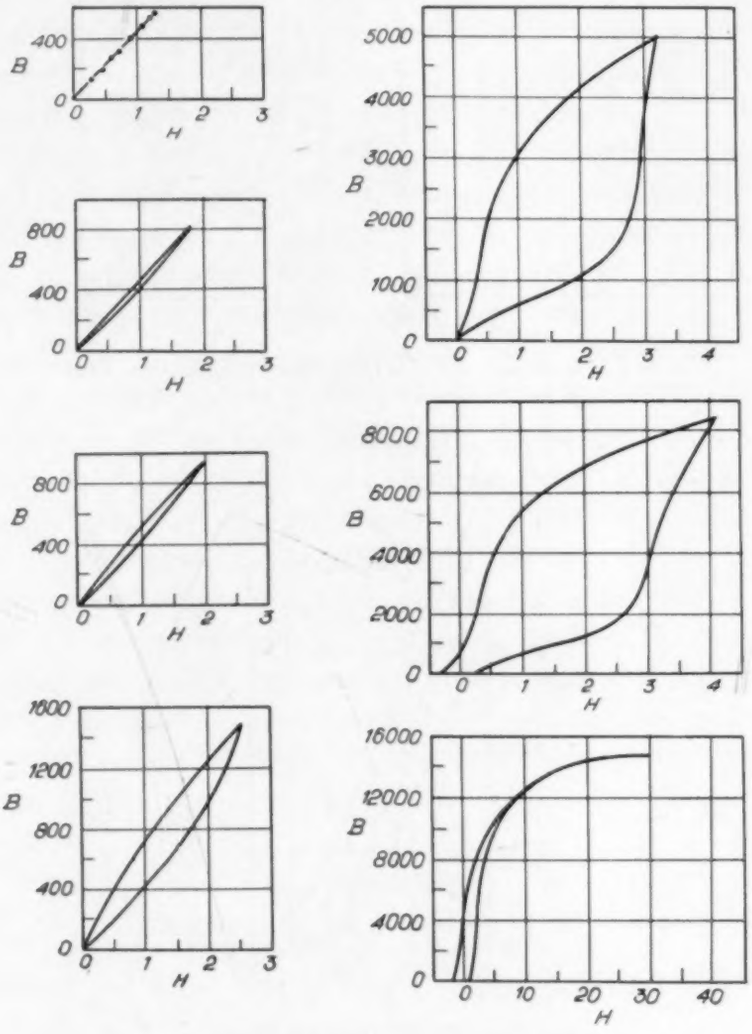


Fig. 17—Perminvar Hysteresis Loops.

A more recent development in Germany resulted in iron-nickel alloys called "isoperms" containing 35 to 55 per cent nickel with some alloying element which tends to precipitate under certain combinations of cold rolling and annealing (33). Aluminum, copper beryllium, manganese and titanium, have been used with varying success. The best alloy contains 40 to 45 per cent nickel, 45 to 50 per cent iron, and 5 to 15 per cent copper. The alloy is first dras-

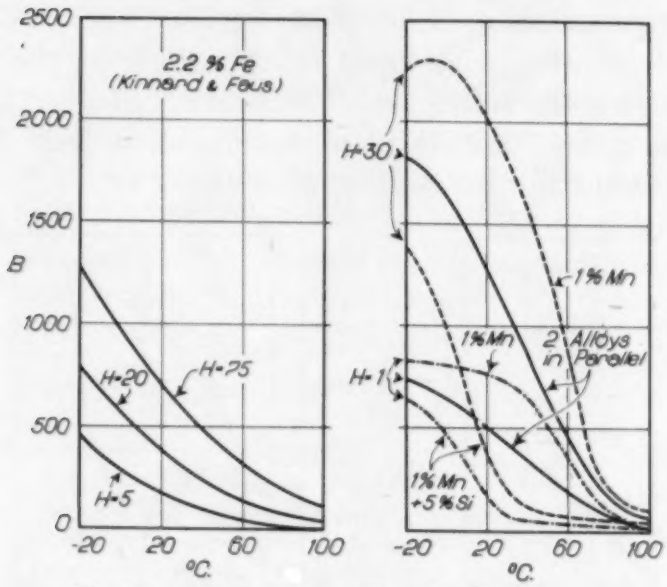


Fig. 18—Monel Type of Magnetic Temperature Compensators 70 Per Cent Nickel Plus 30 Per Cent Copper.

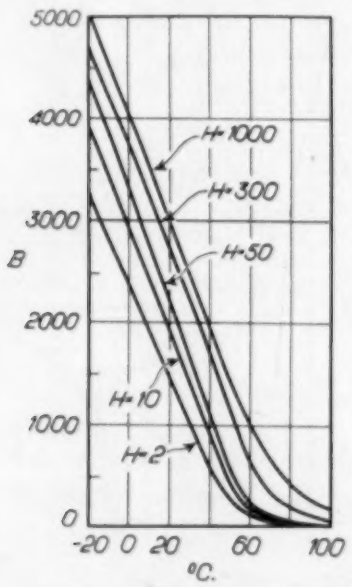


Fig. 19—30 Per Cent Nickel Type of Magnetic Temperature Compensators.

tically cold-rolled, then quenched from a high temperature, further cold-rolled, and finally annealed, a treatment by which the copper is precipitated in such a way as to produce a preferred arrangement of the iron-nickel lattice, resulting in very low retentivity and constancy of permeability (50 to 60) over a wide range of H (0 to 100 oersteds).

Alloys for Magnetic Temperature Compensation—Because of

the fact that the magnetic permeability of iron and iron alloys decreases with temperature (except for low values of H) the reading of electrical meters that depends upon the flux produced by a constant voltage supply or by a certain load current, such for example as watthour meters, decreases with the ambient temperature. To compensate for such errors it is customary to shunt a certain amount of the magnetic flux around the moving part of the meter by means of an alloy having an unusually high magnetic temperature coefficient between 0 and 100 degrees Cent., so that, as the ambient temperature increases, the amount of the shunted flux decreases, forcing more of the flux through the moving member than otherwise would be the case. By proper proportioning of the parts, it is thus possible to compensate almost completely for the temperature changes. Alloys for such purposes are essentially of two types:

(1) The nickel-copper (monel) type having a composition around 70 per cent nickel + 30 per cent copper with certain admixtures, such as iron (General Electric Company's calmalloy (34) containing about 2 per cent iron) or manganese (Westinghouse Alloy containing about 1 per cent manganese with or without a small amount of silicon or these two alloys in parallel) (35).

Characteristic curves are shown for these alloys in Fig. 18.

(2) The nickel-iron type containing around 30 per cent nickel with a small amount of manganese. Such an alloy is Krupp's thermoperm (36) curves for which are shown in Fig. 19, nearly straight lines for all values of H from low temperatures up to 60 degrees Cent. and higher temperature coefficients than for the monel type of alloy.

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INTERNAL STRESSES IN PISTON RODS OF A LARGE DIESEL ENGINE OCEAN LINER

By George Sachs

Abstract

This paper resulted from an investigation on the mechanical breakdown of an ocean liner which attracted considerable attention several years ago. The fatigue failure of 5 out of 24 piston rods was particularly unexpected because for the first time, a heat treated high strength steel had been used instead of the normal soft quality. A striking difference between the two materials was found regarding the magnitude of internal stresses. The heat treated steel contained stresses up to 50,000 pounds per square inch whereas the soft steel was found to be stress-free. A number of methods were tried in order to determine the internal stresses and to find a correlation between the fatigue failures and the stresses. A method previously developed by the author yielded accurate and complete results. The fatigue failures started from the points where internal tensile stresses had their peak. However, the presence of internal stresses was not the only factor which accelerated the fatigue failure; the presence of a radial cooling bore and corrosion by the coolant also participated in the observed radical reduction of the fatigue resistance.

A SHORT time after leaving harbor the diesel engines of a large ocean-going liner stopped working. Upon investigation it was discovered that two out of the four diesel engines had serious failures in the piston rods. Five piston rods were broken and the remaining seven showed beginning cracks. The other two engines were apparently free from failures. Each piston rod broke at the transverse outlet hole for the coolant. A broken surface is shown in Fig. 1. The concentric zones are typical of a fatigue rupture. The remainder of the fracture is partly damaged by the movements of the engine after the failures occurred. The piston rods with cracks as in Fig. 2 showed similar cracks in the intake hole as well as in the outlet hole. Fig.

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Fig. 1—Broken Surface of Piston Rod. Scale 1 to 2.5

3 shows such a crack in a piston rod, which broke during the tests.

The calculated stresses in the piston rods were very low. Dividing the load by the cross section reduced by the hole gives ± 3.2 kilograms per square millimeter (4550 pounds per square inch) vibration stresses. Taking into consideration the stress-increasing effect of the transverse hole the stresses may be as high as ± 8 kilograms per square millimeter (11,400 pounds per square inch).

The material used was a heat treated crucible steel with 0.7 per cent carbon, 0.3 per cent silicon, 0.6 per cent manganese, 0.015 per cent phosphorus, and 0.04 per cent sulphur. The mechanical properties were: tensile strength 69.9 to 74.4 kilograms per square millimeter (100,000 to 105,000 pounds per square inch), yield point

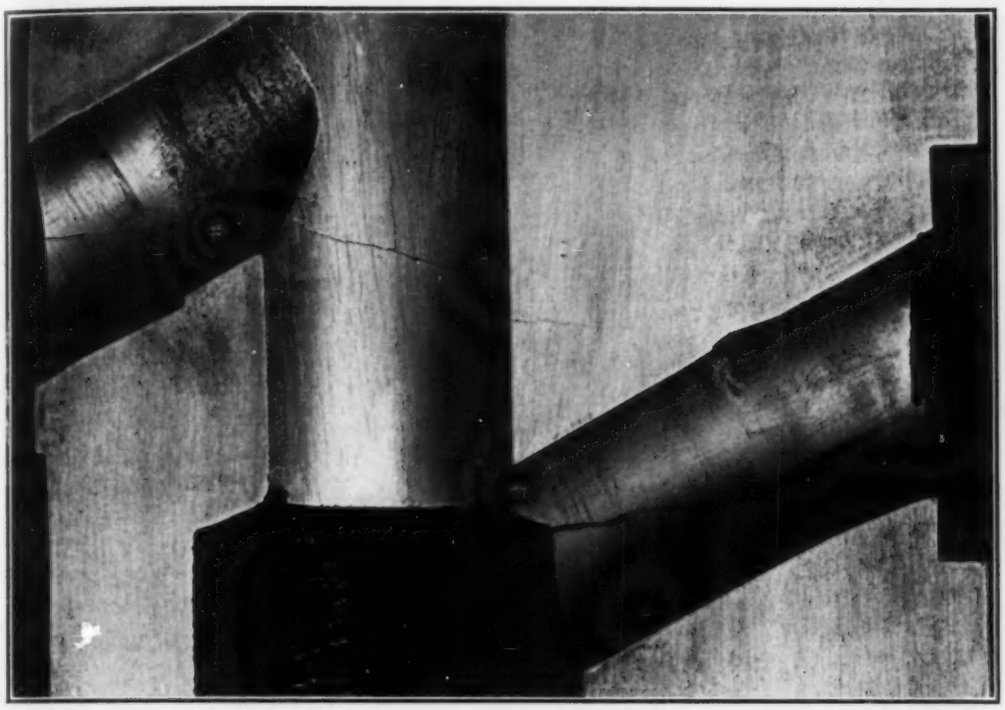


Fig. 2—Piston Rod Section Showing Fatigue Cracks in Both Intake and Outlet Holes. Scale 1 to 2.5.

28.6 to 42.9 kilograms per square millimeter (40,000 to 61,000 pounds per square inch), elongation 17 to 19 per cent, reduction of area 38 to 53 per cent, fatigue limit 35.6 to 40.7 kilograms per square millimeter (50,000 to 58,000 pounds per square inch), Brinell hardness 208 to 222 and Young's Modulus 21,000 kilograms per square millimeter (30,000,000 pounds per square inch). The structure was composed of spheroidized cementite. The material was particularly chosen because of its high mechanical properties instead of a normally used soft open-hearth steel. The big forgings were quenched in oil from 1560 degrees Fahr. and drawn at 1240 degrees Fahr. From the drawing temperature the rods were probably quenched again. The forgings were then straightened and machined to size, including the boring of the longitudinal and transverse holes for the coolant.

Considering the possible sources of this serious failure a hitherto disregarded factor, the presence of internal stresses, was followed up. Before this investigation was made, there was little known about internal stresses in big forgings. The presence of high internal stresses in the present case could easily be shown; but it was rather difficult to determine their intensity and distribution. The different methods of approximation (1)[1] did not give sufficiently accurate and

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

consistent results. Only by the method, developed by the author (2), was it possible to get a complete picture of the internal strain.

Longitudinal Cutting the Piston Rods

By cutting the piston rods or the forgings along the axis, the two parts warp appreciably (Fig. 4). A piston rod, however, made

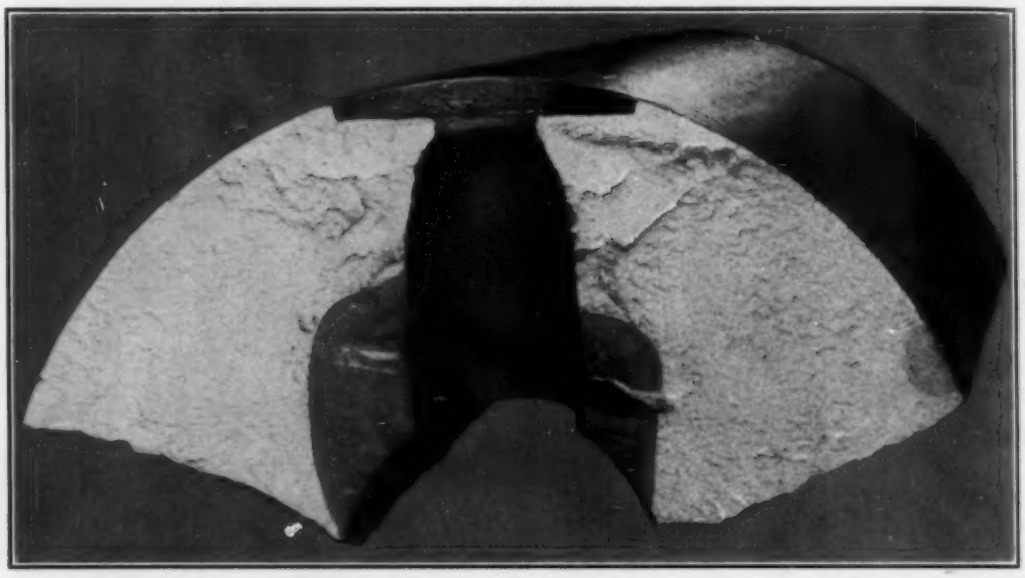


Fig. 3—Piston Rod Showing Fatigue Crack Broken During Cutting in Half. Scale 1 to 2.5.

of carefully annealed open-hearth steel does not warp as in the first case and shows no indication of released internal stresses (Fig. 5).

The deflections of the two parts of one piston rod, which broke in cutting (Fig. 4), are given in Fig. 6. According to these figures the curvature of each part is very near that of a circle; the deflection of a length of 1000 millimeters (40 inches) being about 1.9 millimeters (0.07 inch). A second piston rod had about the same deflection, a third one about 2.4 millimeters (0.1 inch) per 1000 millimeters. In each case the deflection decreased near the piston.

The warping of these large forgings indicates clearly the existence of high internal stresses. However, their real quantity cannot be determined accurately this way. There is little difficulty in calculating the bending moment, which is necessary to bring the distorted parts back to their straight position before cutting. But to transform the bending moment into stresses is not possible without an additional assumption regarding their distribution. This assumption would be wrong in any case because the variation of the stresses

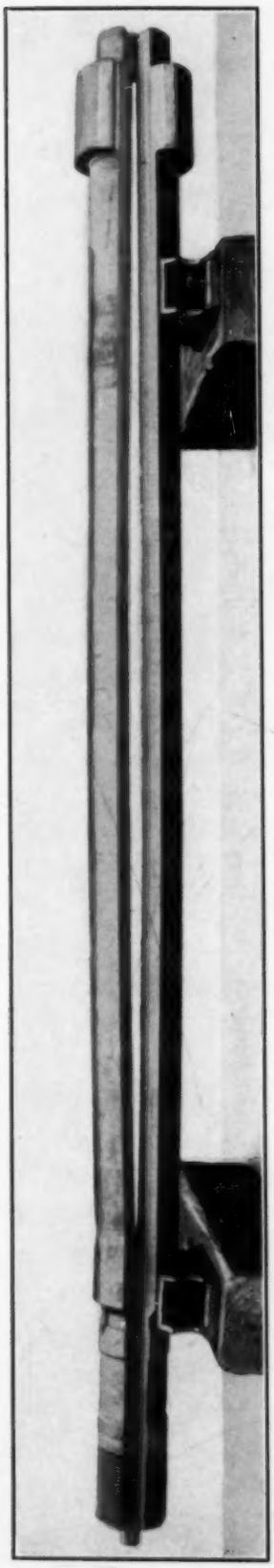


Fig. 4—Tempered Crucible Steel Piston Rod Cut in Half, Warped by Release of Internal Stresses and Broken at a Fatigue Crack. Scale 1 to 30.

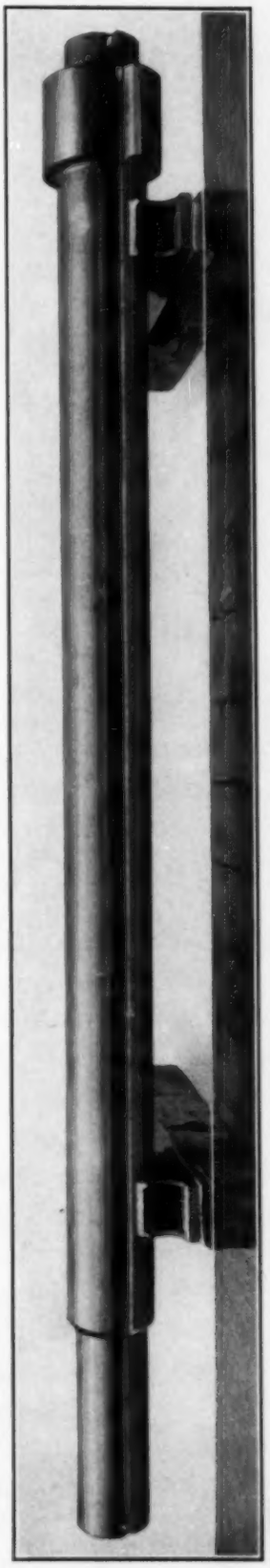


Fig. 5—Soft Steel Piston Rod, Cut in Half and Free from Internal Stresses. Scale 1 to 30.

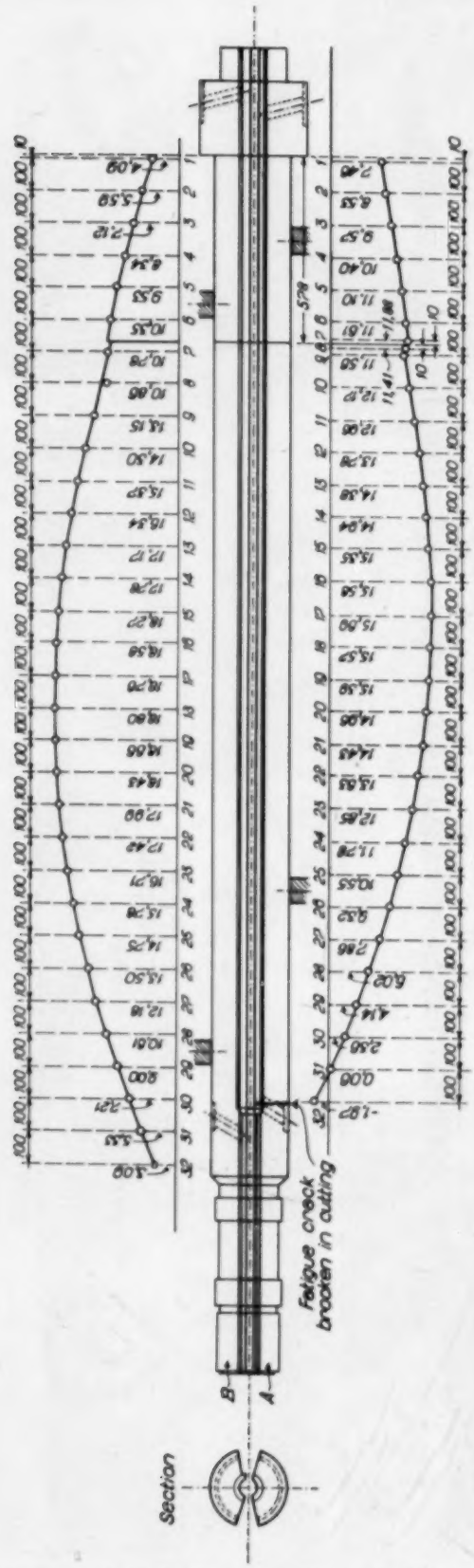


Fig. 6—Amount of Deflection of a Piston Rod Cut in Half.

Table I
Changes in Length of a Piston Rod in Turning Off Layers
(Length of test piece = 1200 mm—48")
(Length of turned part = 1000 mm—40")

No. of Measurement	Diameter mm	Measurements Near Hole: Length L mm	Change in Length $\Delta L = L - L_o$ mm	$\frac{\Delta L}{L_o}$ 10^{-5}	Measurements Near Surface: Length L mm	Change in Length $\Delta L = L - L_o$ mm	$\frac{\Delta L}{L_o}$ 10^{-5}
0	235	1199.85_3	....	..	1199.82_8	....	..
1	225	1199.82_5	-0.02_8	2_8	1199.79	-0.13_8	13_8
2	215	1199.74	-0.11_3	11_3	1199.72	-0.20_8	20_3
3	205	1199.64_5	-0.20_8	20_8	1199.63_5	-0.29_3	29_3
4	195	1199.57_7	-0.27_0	27_0	1199.55_3	-0.37_5	37_5
5	185	1199.51	-0.34_3	34_3	1199.47	-0.45_8	45_8
6	175	1199.40_3	-0.45_3	45_3	1199.36	-0.56_8	56_8
7	165	1199.27_3	-0.58_0	58_0	1199.27_8	-0.65	65
8	155	1199.22_5	-0.62_8	62_8	1199.17_5	-0.75_3	75_3
9	145	1199.16	-0.69_3	69_3	1199.11_5	-0.81_3	81_3
10	135	1199.10_3	-0.75_0	75_0	1199.03_8	-0.89	89
11	125	1199.02_8	-0.82_5	82_5	1199.96_5	-0.96_3	96_3
12	115	1199.14_5	-0.70_8	70_8	1199.08	-0.84_8	84_8
13	103	1199.25_5	-0.59_8	59_8	1199.19_8	-0.73	73
14	90	1199.56_5	-0.28_8	28_8	1199.52_3	-0.40_5	40_5

with the distance from the axis of the rod is not known and surely is not a simple function. The simplest assumption is that of a linear variation, it may give either too high or too low stress values. Furthermore, it is impossible to take into consideration the influence of the transverse stresses on the longitudinal stresses. Cutting this way releases only a part of the stresses, shown as follows.

Cutting Out a Segment

The stresses can however be eliminated completely if a narrow segment is cut from such a parted piston rod. Doing this with the piston rod shown in Fig. 5 increased the deflection by about 100 per cent to 3.7 millimeters (0.15 inch). The segment was 1000 millimeters (40 inches) long and 30 millimeters (1.2 inches) wide on the outside. Calculating with a linear distribution of stresses and a Young's Modulus of 20,000 kilograms per square millimeter (28,400,000 pounds per square inch) results in tensile stresses of 27.4 kilograms per square millimeter (39,000 pounds per square inch) at the surface of the hole and compression stresses of 19.3 kilograms per square millimeter (28,000 pounds per square inch) at the outside surface. Comparing these figures with the correct ones below shows that they are considerably too low. This difference is caused by neglecting the transverse stresses. This method does not tell anything about the distribution of the stresses outside of the fact that they must give the right sign of the bending moment.

Gradually Reducing the Diameter by Turning

A method to determine not only the amount but also the distribution of the longitudinal stresses consists in reducing gradually the diameter of a certain length and measuring the change of this length

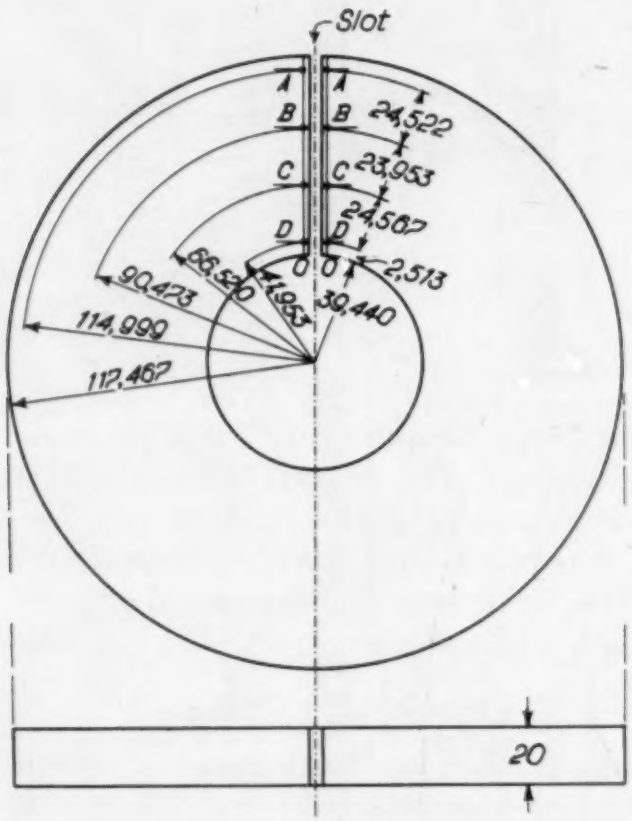


Fig. 7—Scheme for Cutting a Slice from a Piston Rod and Cutting Radially to Measure the Distortion by Release of Internal Stresses.

after each turning operation (3), (4). However, this method also disregards the transverse stresses and gives in most cases stress values that are too low (6). Another difficulty was met, when this method was used in the present case. Measuring the change in length of a test piece 1200 millimeters (48 inches) long, it was found according to Table I that these variations were different at the surface and at the hole by about 10 per cent. Besides a part of the stresses have already been eliminated in cutting the test piece off of the forging.

A few further experiments were carried out to measure the length of a test piece of 400 millimeters (16 inches) with a microscope. But no reliable figures could be obtained by this method.

Table II

Deformations of a Cut Off Slice of 10 mm = 0.4" Thickness After Radial Slotting

See Fig. 7

	Radius	Diameter d = 2r Before Slotting	Diameter d = 2r After Slotting	Change of Diameter		Distance A — A, B — B, Etc. Before After Slotting		Change	Length of Segment	Change	Total Change	Internal Stress
	r	d_v	d_n	$\Delta d = d_n - d_v$	$\frac{\Delta d}{d_v}$	b_v	b_n	$\Delta b = b_n - b_v$	$L = \pi d_v - b_v$	$\frac{-\Delta b}{L}$	$^*)\lambda = \frac{\Delta b}{L} - \frac{\Delta d}{d_v}$	$s = E\lambda\,^\dagger)$
	mm	mm	mm	mm	10^{-5}	mm	mm	mm	mm	10^{-5}	10^{-5}	kg/mm²
Outside	117.467	234.934	234.683	−0.251	.....	.....	.....	.....	...	.....	.....	.....
A — A	115.00	(230.00)	.....	−0.250*)	−108.6	9.911	8.726	−1.185	711	166.7	+58	11.6
B — B	90.47	(180.94)	.....	−0.245*)	−135.4	9.917	8.984	−0.934	558	167.5	+32	6.4
C — C	66.52	(133.04)	.....	−0.238*)	−178.8	9.908	9.234	+0.673	408	165.0	−14	− 2.8
D — D	41.95	(83.90)	.....	−0.232*)	−276.5	10.079	9.642	−0.435	253	172.0	−104	−20.8
Inside	39.44	78.88	78.649	−0.231	.....	.....	.....	.....	...	.....	..	....

*) Interpolated.
†) E = 20000 kg/mm²

Obviously the whole measuring device was warping irregularly during the measurements.

Radial Slotting of a Cut-off Slice

None of the above methods of approximation give any idea about the amount and distribution of the transverse stresses in the tangential direction. A simple method to show the presence of such stresses in tubular rods consists in cutting off a thin slice and slotting through the axis, as shown in Fig. 7. Table II gives the deformations of a slice of 20 millimeters (0.8 inch) thickness, calculated from the changes of distance between corresponding points A-A, B-B, etc., of two radii close to the slot. By multiplying these deformations by the Young's Modulus some approximate figures for the tangential stresses are obtained. This simple calculation gives for one piston rod according to Table II near the outside surface a compression stress of 11.6 kilograms per square millimeter (16,500 pounds per square inch) and near the longitudinal hole a tensile stress of 21 kilograms per square millimeter (29,600 pounds per square inch). In another piston rod about 25 per cent lower stresses were found. This method shows there are also high transverse stresses present. They are less than half as high as they are actually.

Gradually Increasing the Longitudinal Hole by Boring

A method to determine the stresses in cylinders and thick-walled tubes in a fairly complete way was developed by the author (2). The method is bound to the important condition that the state of stress has rotational symmetry. This assumption is met in the present case.

In the author's method a test piece of sufficient length—at least three times the diameter—is cut from the rod to be tested. This test piece is bored out through the entire length in small steps.

At each step, which is determined by the cross section f of the hole, the change of the initial length l_o and of the initial diameter d_o of the rod is measured. The points of measurements have to be kept away from the ends of the test piece sufficiently far—a distance approximately the size of the diameter—to give undisturbed figures.

A complete experiment was carried out by this method with a test piece of 1100 millimeters (44 inches) length, cut from a piston

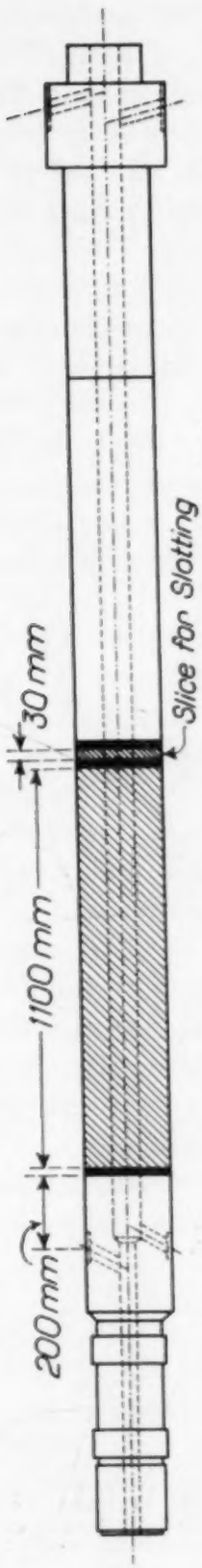


Fig. 8—Scheme of Test Pieces for Measuring Internal Stresses in a Piston Rod.

rod according to Fig. 8. The outside diameter was measured with a micrometer at polished and marked spots 300 millimeters (12 inches) away from each end in four different directions. To get the changes of the length sufficiently accurate, two rings were soldered upon the rod about 200 millimeters (8 inches) away from the ends. Their distance of 700 millimeters (28 inches) was measured at eight corresponding points with a micrometer gage. The wall thickness was measured at each end and at eight points. This dimension does not have to be as accurate as the other ones.

In taking the actual measurements, it was observed that these figures decreased continuously, corresponding to a slight increase in temperature of the measuring device by the radiation of the human body. Repeating these measurements until these changes remained within $\pm$ 0.003 millimeter gave reproducible figures.*

In a state of rotational symmetry the individual figures of one set of measurements should be identical. In the present case the normal variations did not exceed $\pm$ 3 per cent; this proves that the state is one of rotational symmetry. Only in the few last measurements—approaching a very thin wall of the remaining shell—the variations increased to about $\pm$ 30 per cent of the total deformation of 0.6 per cent (that means 0.6 $\pm$ 0.2 per cent).

The boring operations were carried out on a big horizontal lathe with small steps and excessive cooling. The change of length was followed up during the operation with a dial micrometer attached to the rod by shells. After finishing one boring operation the dial indicated regularly the decrease of length in approaching again the room temperature. To get as far as possible to a state of equilibrium, the measurements were therefore taken early in the morning the next day after the boring operation. During the whole process the test piece was not removed from the lathe.

The results of the measurements are given in Table III and Fig. 9. The author's method uses the expressions:

$$\Lambda = \lambda + \mu\,\delta$$
$$\Theta = \delta + \mu\,\lambda$$

$$\text{with: } \lambda = \frac{\Delta l}{l_o} \quad (\Delta l = \text{change in length in mm.})$$

*One experiment was also carried out to measure the deformations with a microscope, which was mounted on an I-beam. But the variations hereby were as high as $\pm$ 0.05 millimeter (0.002 inch) and much too high for the present problem. It seems as if the whole device warps through the heat of the human body.

$$\delta = \frac{\Delta d}{d_o} \quad (\Delta d = \text{change in diameter in mm.})$$

μ = Poisson's ratio = 0.3

These are also given in Table III and Fig. 9. The longitudinal stresses s and the tangential stresses t have to be calculated according to the formulae:

$$s = \frac{E}{1-\mu^2}\left[(f_b - f)\frac{d\Lambda}{df} - \Lambda\right]$$

$$t = \frac{E}{1-\mu^2}\left[(f_b - f)\frac{d\Theta}{df} - \frac{f_b + f}{2f}\Theta\right]$$

(E = Young's Modulus, f_b = cross section of the solid rod, f = cross section of the hole)

The radial stresses were not followed up as they are normally of minor importance.

With the actually measured figures Λ and Θ in Table III the

Table III

Changes in Length and Diameter of a Test Piece (Cut Off a Piston Rod) During Boring

Length of test piece = 1100 mm = 44″)
(Measured length l_o = 699.9 mm = 28″)
(Diameter d_o = 234.1 mm = 9.6″)

Measurement	Diameter of Hole d	Cross Section of Hole $f = \frac{\pi d^2}{4}$	Change of Length Δl	$\lambda = \frac{\Delta l}{l_o}$	Change of Outside Diameter Δd	$\delta = \frac{\Delta d}{d_o}$	$\Lambda = \lambda + \mu\delta$	$\Theta = \delta + \mu\lambda$
	mm	mm²	mm	10^{-5}	mm	10^{-5}	10^{-5}	10^{-5}
0	78.07	47 90	.....	..	.....	..	...	..
1	79.93	50 20	$+0.004_2$	$+\ 0_6$	-0.001_4	$-\ 0_6$	$+\ 0_4$	$-\ 0_4$
2	90.37	64 10	$+0.015_1$	$+\ 2_2$	$+0.018_0$	$+\ 7_7$	$+\ 4_5$	$+\ 8_4$
3	100.18	78 90	$+0.038_3$	$+\ 5_5$	$+0.029_8$	$+12_7$	$+\ 9_3$	$+14_4$
4	102.52	82 50	$+0.043_5$	$+\ 6_2$	$+0.032_6$	$+13_9$	$+\ 10_4$	$+15_8$
5	113.50	101 10	$+0.091_8$	$+13_1$	$+0.041_0$	$+17_9$	$+\ 18_5$	$+21_8$
6	121.86	116 70	$+0.142_4$	$+20_4$	$+0.053_5$	$+22_8$	$+\ 27_2$	$+28_9$
7	132.31	137 90	$+0.208_4$	$+29_8$	$+0.065_9$	$+28_1$	$+\ 38_2$	$+37_0$
8	140.05	154 20	$+0.247_6$	$+35_4$	$+0.073_3$	$+31_3$	$+\ 44_3$	$+41_9$
9	143.52	162 00	$+0.275_0$	$+39_3$	$+0.076_7$	$+32_7$	$+\ 49_1$	$+44_5$
10	150.45	177 80	$+0.327_1$	$+46_7$	$+0.086_9$	$+37_1$	$+\ 57_3$	$+51_2$
11	158.17	196 50	$+0.383_1$	$+54_7$	$+0.094_7$	$+40_4$	$+\ 66_8$	$+56_8$
12	165.24	214 50	$+0.423_1$	$+60_4$	$+0.103_0$	$+44_0$	$+\ 73_8$	$+62_1$
13	172.22	233 00	$+0.475_4$	$+67_9$	$+0.107_8$	$+46_0$	$+\ 81_7$	$+66_4$
14	176.75	245 00	$+0.517_2$	$+73_8$	$+0.114_5$	$+49_0$	$+\ 88_5$	$+71_1$
15	182.02	261 00	$+0.540_8$	$+77_2$	$+0.116_3$	$+49_7$	$+\ 92_1$	$+72_9$
16	186.45	273 00	$+0.570_9$	$+81_5$	$+0.117_7$	$+50_3$	$+\ 96_8$	$+74_8$
17	193.03	296 00	$+0.597_4$	$+84_4$	$+0.121_4$	$+51_9$	$+101_0$	$+77_5$
18	200.59	316 00	$+0.624_8$	$+89_3$	$+0.126_1$	$+53_9$	$+105_5$	$+80_7$
19	206.28	334 00	$+0.649_4$	$+92_8$	$+0.132_8$	$+56_8$	$+109_8$	$+84_6$
20	210.63	348 00	$+0.657_4$	$+93_9$	$+0.135_8$	$+57_9$	$+111_3$	$+86_1$
21	215.87	365 00	$+0.683_4$	$+97_6$	$+0.140_5$	$+60_0$	$+115_6$	$+89_3$
22	219.73	379 00	$+0.678_5$	$+96_9$	$+0.148_6$	$+63_5$	$+115_9$	$+91_6$

Poisson's ratio. $\mu = 0.3$

stresses cannot be calculated very accurately, as it is necessary to form differences. It is therefore more accurate to use in their place the figures given by the trend line in Fig. 9, which equalizes the unavoidable variations of the actual measurements.

The result of the calculation is reproduced in Fig. 10. The longitudinal tensile stresses have their maximum value of 32 kilo-

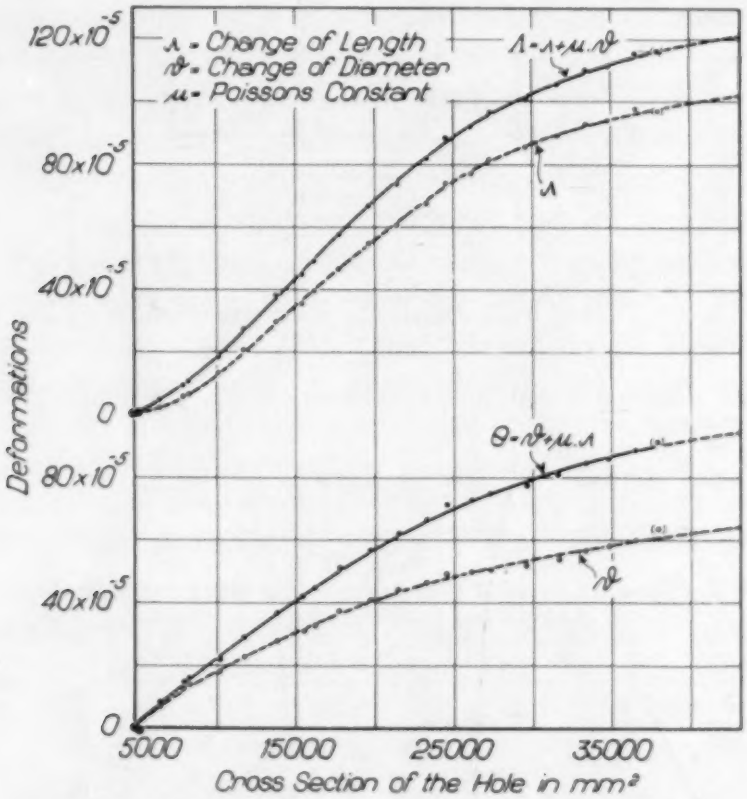


Fig. 9—Deformation of a Test Piece Cut from a Piston Rod and Machined Gradually from Inside.

grams per square millimeter (46,000 pounds per square inch) at a point about 15 millimeters (0.6 inch) away from the surface of the hole. The tangential tensile stresses have their maximum value of 37.5 kilograms per square millimeter (54,000 pounds per square inch) directly at the surface of the hole.

A second experiment was carried out with a piece of the same size, which was cut from a broken piston rod. The exact data of failure for this piston rod is not known, so that it was running for a while after the failure occurred. The broken surface was smoothened by the hammering action of the two parts and this had also increased the diameter by about 0.8 per cent. The stresses in this case only amounted to about 10 per cent of the stresses in the unbroken piston

rod. The large difference is obviously caused by the compression of the rod after the failure occurred, as it could be shown with small test pieces that uniform deformations, elongations or compressions, reduce internal stresses to low values (*7*).

Fatigue Cracks and Internal Stresses

This investigation has shown that in heat treated steel forgings of large sizes internal stresses up to 60 per cent of the tensile strength

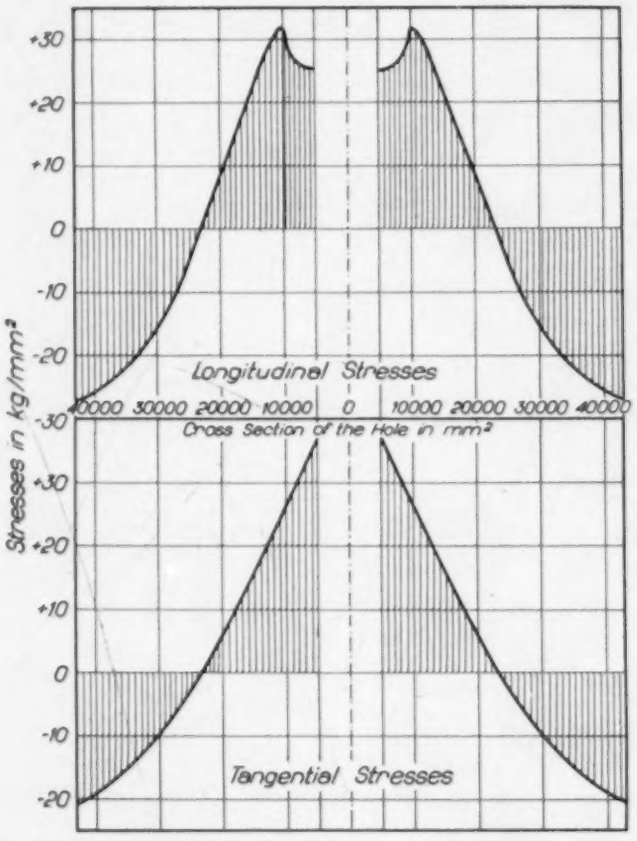


Fig. 10—Internal Stresses in a Piston Rod.

and of the same magnitude as the fatigue strength may be present. To get the proper amount and distribution of these stresses a somewhat complicated method has to be used. Simpler methods of approximation may be useful for controlling the production (8), but they generally give too low values of the stresses and do not reveal their actual distribution.

At first it seems only natural to attribute the fatigue failures of the piston rods exclusively to these high internal stresses. Addition-

ally, this seems to be confirmed by the fact that according to Fig. 2 the fatigue cracks started generally from a point on the surface of the transverse hole, which is a certain distance away from the longitudinal hole. This corresponds to the result of the present investigation, that the highest longitudinal tensile stresses were also found in the same region. Adding small vibration stresses to such high internal stresses may cause fatigue cracks to start rapidly.

However, fundamental investigations carried out, partly caused by the herein described failures, have revealed a few facts, which reduce the importance of internal stresses. It was found that vibrations decrease continuously the amount of internal stresses (9) and that the corrosive action of the coolant is another well-known factor, which speeds up appreciably a fatigue failure (10). The transverse hole with its rough surface is a further unfavorable feature.

Therefore the failure has eventually to be attributed to a combined action of three factors.

1. High internal stresses caused by unsuitable heat treatment.
2. Stress-increasing changes of cross section, caused by unfavorable design.
3. Reduction of fatigue strength by corrosion, caused by unsuitable cooling.

A few experiments were also carried out to find the actual source of these internal stresses (6). Stresses of this magnitude can form easily in forgings of any size if these are quenched in water or oil from temperatures above 900 degrees Fahr. (11).

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ISOTHERMAL TRANSFORMATION IN STEELS

By Edmund S. Davenport

Abstract

The development and fundamental significance of isothermal transformation investigations as applied to the heat treatment of steel is briefly reviewed, and the major effects of alloying elements as revealed by such studies are outlined by means of isothermal transformation diagrams ("S"-curves). The effect of individual elements, C, Mn, Ni, Cr, Mo, V and Co, is first discussed and this is followed by the presentation of the isothermal transformation diagrams of several typical alloy steels of the S.A.E. series, 0.40 per cent carbon grade.

With the exception of cobalt, all of the alloying elements investigated retard the transformation of austenite in the Ar' range, provided the element is in real solid solution in the austenite prior to transformation. Chromium, molybdenum and vanadium are most effective in this respect, with manganese next in order, while nickel and carbon exert a smaller, but appreciable, influence.

Many of the 0.40 per cent carbon alloy steels investigated have isothermal transformation curves which scarcely resemble the letter "S" and from the standpoint of both theory and practice these alloy steel curves have quite different implications from the now-familiar S-curve for eutectoid carbon steel.

The hardness and microstructure of the S.A.E. steels, as isothermally transformed at several different temperature levels down to 600 degrees Fahr., are discussed in some detail and, insofar as possible, these observations are correlated with the corresponding trends as observed in carbon steels.

Introduction

THE honor of being selected as the 14th Campbell Memorial Lecturer to perpetuate the memory of Edward DeMille Campbell is one which I appreciate highly. I had not the privilege, enjoyed by many former Campbell Lecturers, of studying under Professor

This is the Fourteenth Edward DeMille Campbell Memorial Lecture, presented by Edmund S. Davenport, metallurgist, Research Laboratory, United States Steel Corp., Kearny, N. J. The lecture was presented at the Twenty-First Annual Convention of the Society, held in Chicago, October 23 to 27, 1939.

Campbell or even of knowing him personally. However, his reputation as a leader and trainer of young men and his attainment of a high place in his chosen profession in spite of a physical handicap, which to most men would have spelled defeat and obscurity, will always stand as a source of inspiration to students and workers in the field of metallurgy.

In common with many of his contemporaries, Professor Campbell devoted much of his effort to the investigation of various aspects of the constitution of steel as revealed by studies involving, on the one hand, conditions of presumed equilibrium, or on the other hand, conditions in which the influence of time and of temperature could not be readily separated or evaluated. In recent years it has become increasingly evident that if we are to get at the fundamentals of the subject of heat treatment of steel, we shall have to make a systematic effort to disentangle the influence of time and of temperature by studying each one separately; in order to do this, one factor (time or temperature) must be held constant while the other is varied in some predetermined manner. To study the effect of continuous cooling fails to meet these requirements, since, with any given cooling rate, both time and temperature are changing simultaneously and it is utterly impossible to evaluate the separate influence of either factor.

Such considerations led us to investigate the constant-temperature, or isothermal, transformation of austenite. This work was started at the Research Laboratory of the United States Steel Corporation just ten years ago this month and has been pursued there continuously since that time. The so-called "S-curve" diagram, which summarizes the observations in condensed form, is the theme of today's lecture; it depicts the time required for the breakdown of austenite to ferrite and carbide at any constant temperature below the equilibrium transformation range and embodies, we believe, the fundamentals of the subject of heat treatment insofar as the transformation of austenite is concerned. I propose, therefore, to review rather briefly the development and significance of isothermal transformation studies and then to pass on to a discussion of the influence of alloying elements in steel as revealed by such studies.

Technique of Isothermal Transformation Studies

Several means for following the progress of isothermal trans-

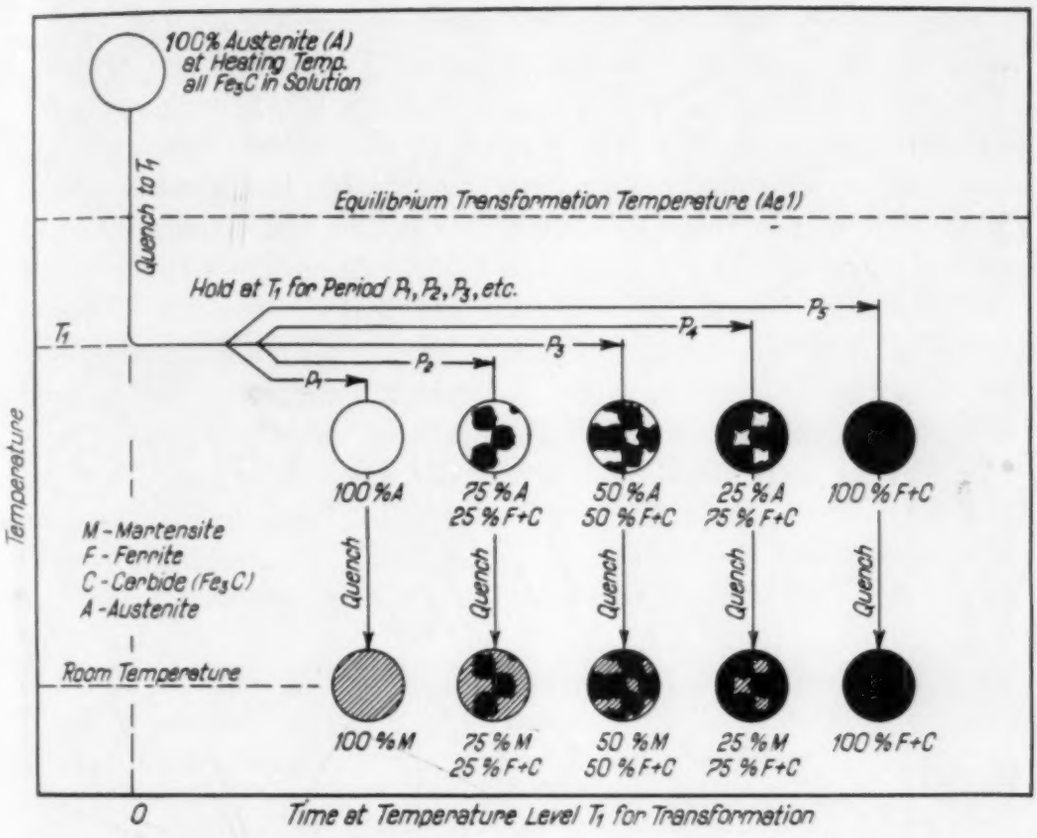


Fig. 1—Schematic Representation of Heat Treating Operations Involved in Preparing Specimens for Estimating Progress of Isothermal Transformation by the Metallographic Method.

formation are available, for instance, by metallographic examination of specimens taken from a constant temperature bath at appropriate intervals, or by measurement of the change of length of a specimen at temperature, or even by hardness or magnetic measurements. These methods all yield substantially the same result, but the most informative is the metallographic method since, in effect, it permits us to see the transformation process while it is going on and hence to gain some knowledge of its mechanism and of the structure of the product. I shall, therefore, briefly outline the experimental technique of this method even though it has already been described in detail elsewhere (5), (43).[1]

The principle of the method is shown schematically in Fig. 1. Individual specimens of suitably small dimensions are first rendered austenitic, then rapidly transferred to a liquid bath maintained at the particular temperature level (T_1) under investigation, held at that

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

constant temperature for a predetermined time period (p_1, p_2, p_3, etc.), withdrawn and immediately quenched in cold water or brine. The specimens are subsequently sectioned, polished, etched and examined microscopically. The essence of the method resides in the fact that any untransformed austenite remaining in a given specimen at the end of its sojourn in the constant temperature bath appears as martensite after the final quench in brine. Attention is called to the fact that Fig. 1 is purely schematic and that the amount of transformation shown for each individual specimen is not necessarily that which would be found in such a series in actual practice. Moreover, while only five different holding periods are shown, a much larger number may be required to determine the "beginning" and "end" of visible transformation. The terms "beginning" and "ending" will be used throughout the balance of the lecture to characterize, respectively, the time interval required for the first detectable traces of transformation product to appear and the last detectable traces of austenite to disappear, regardless of the means of measurement employed; thus we shall have occasion to refer to "beginning lines" and "ending lines" in discussing the various charts and diagrams hereafter presented.

Actual examples of the metallographic method as applied at the temperature levels 1300 and 500 degrees Fahr. (705 and 260 degrees Cent.) are shown in Figs. 2, 3 and 4; Fig. 2 illustrates the course of the transformation to pearlite at 1300 degrees Fahr. (705 degrees Cent.) in eutectoid steel, while Fig. 3 shows it at the same temperature level in a hypoeutectoid steel, in which case the pearlite reaction is preceded by separation of proeutectoid ferrite; Fig. 4 depicts what happens at 500 degrees Fahr. (260 degrees Cent.) where the product is the rapid-etching, acicular structure frequently referred to as bainite.

Dilatometric or magnetic measurements and other methods of following the transformation continuously have been used with success (5), (27), (68); these methods, although less dependent upon the judgment of the observer than the metallographic method, give no clue as to the structure of the product formed out of the austenite or as to its mode of formation. Regardless of the method used, the data are usually plotted in the form of curves (39), such as those reproduced in Fig. 5, from which the time corresponding to any stage in the progress of the isothermal transformation at any temperature level may be estimated. An alternative method of plotting,

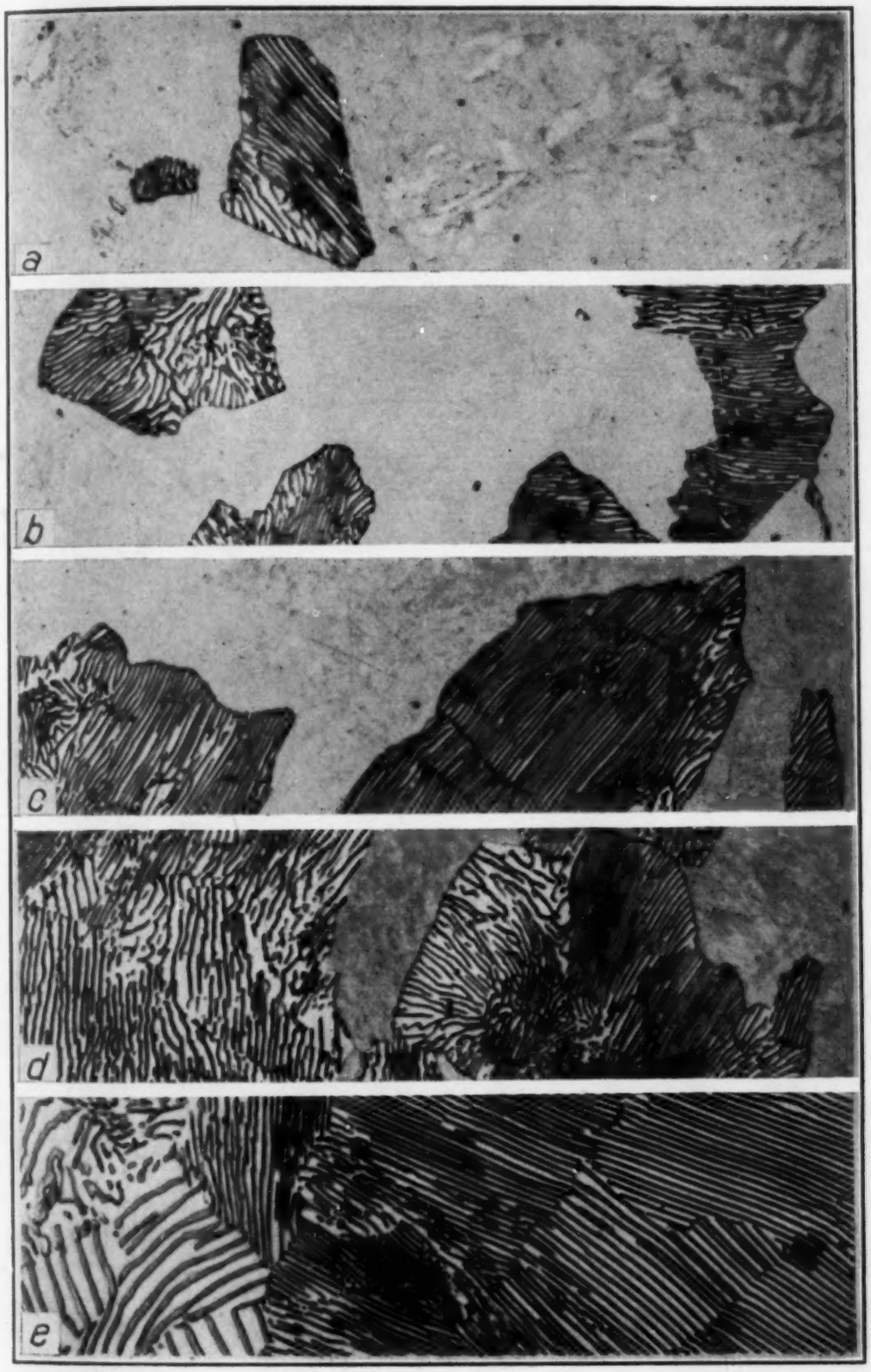


Fig. 2—Example of Metallographic Method as Applied to Transformation of Austenite to Pearlite at 1300 Degrees Fahr. in Eutectoid Steel. Magnification × 1000. (a) 320 Seconds, Transformation Begins; (b) 1150 Seconds, 25 Per Cent Transformed; (c) 1320 Seconds, 50 Per Cent Transformed; (d) 1450 Seconds, 75 Per Cent Transformed; (e) 4000 Seconds, 100 Per Cent Transformed.

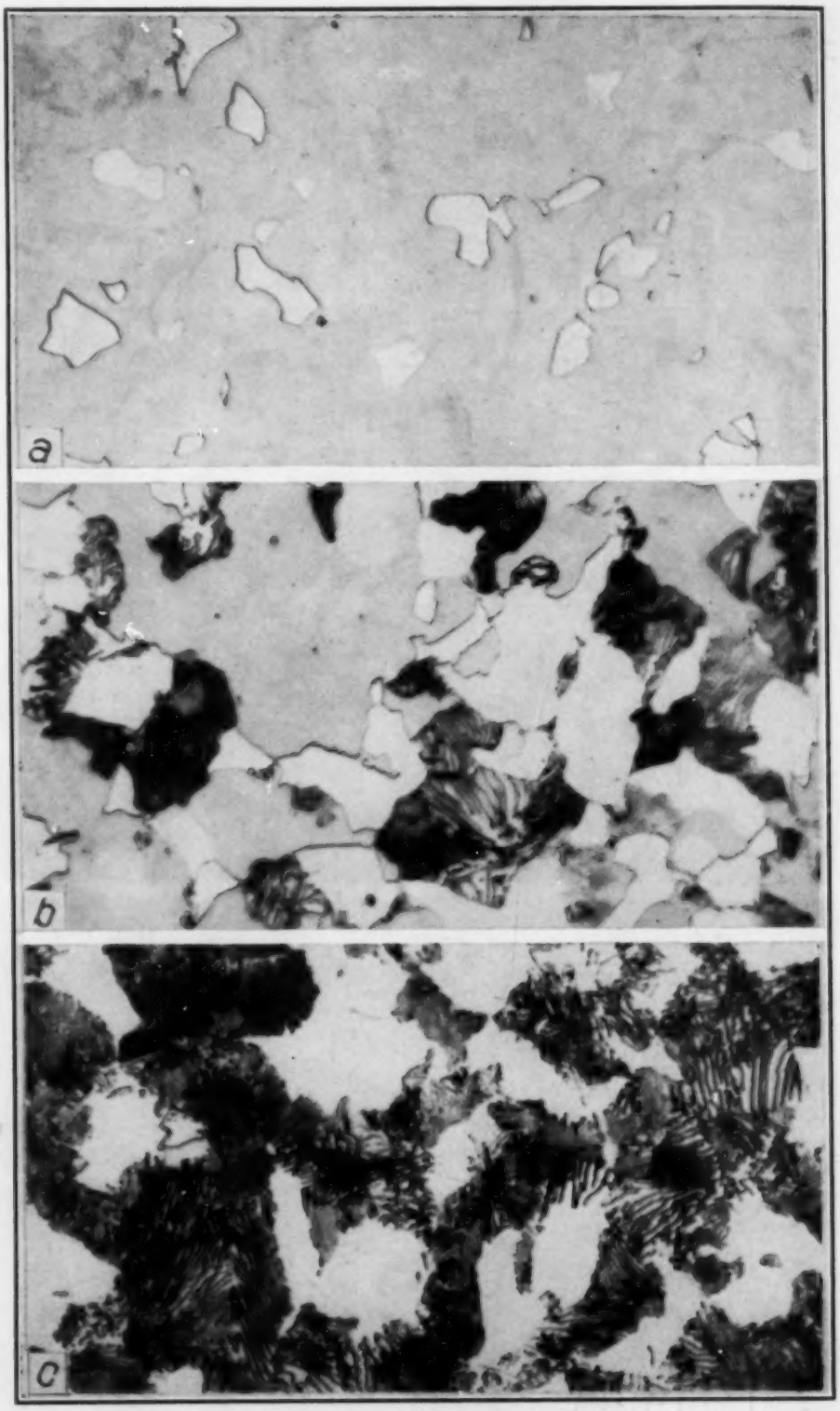


Fig. 3—Metallographic Method as Applied to Transformation of Austenite to Ferrite + Pearlite at 1300 Degrees Fahr. in Hypoeutectoid Steel. × 1000.

(a) 1 Minute Transformation Has Started with Rejection of Proeutectoid Ferrite. (b) 5 Minutes Transformation Proceeds with Continued Rejection of Ferrite Followed by Formation of Pearlite. (c) 30 Minutes Transformation Goes to Completion by Continued Formation of Pearlite.

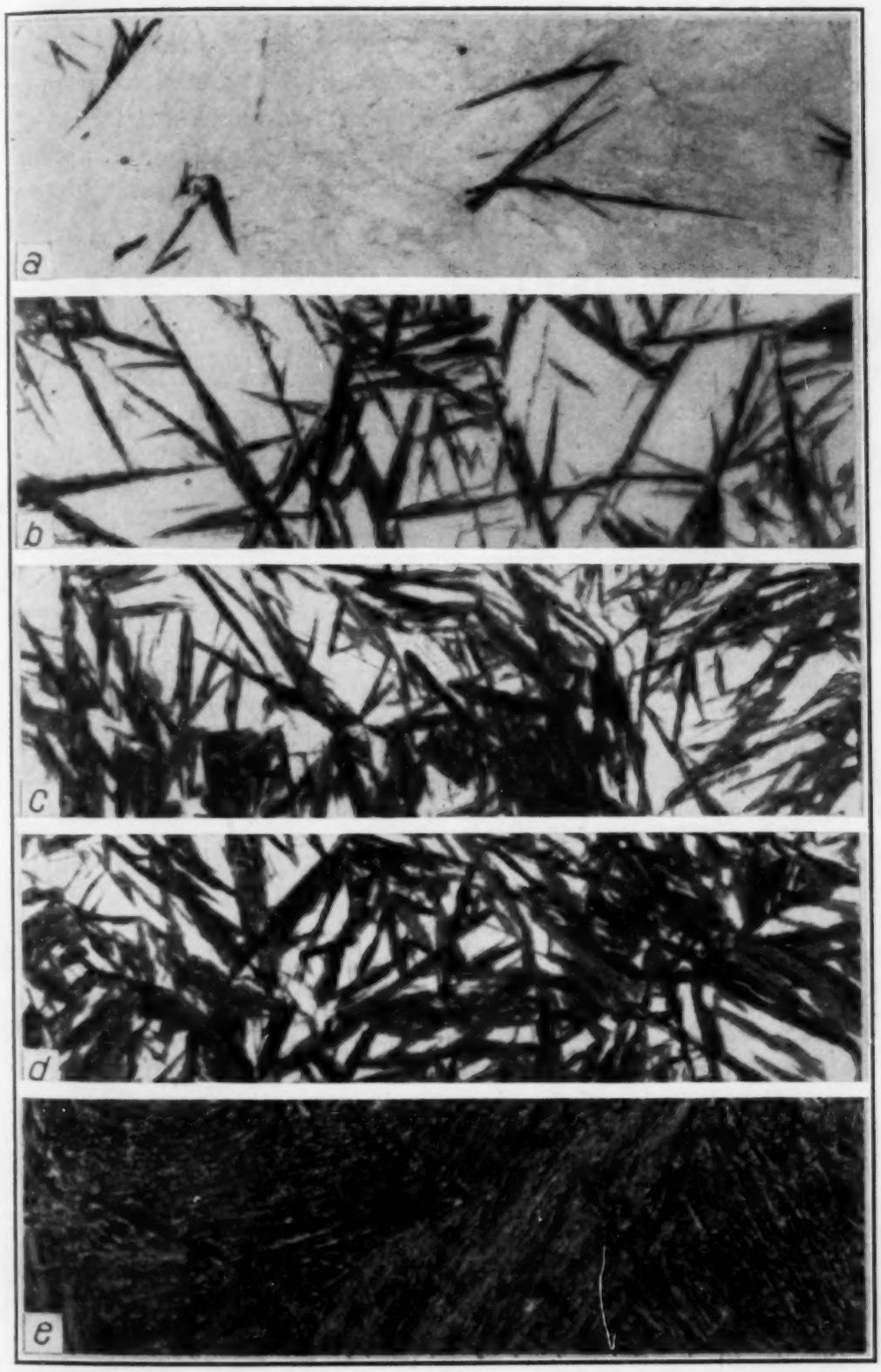


Fig. 4—Example of Metallographic Method as Applied to Transformation of Austenite to Bainite at 500 Degrees Fahr. in Eutectoid Steel. Magnification × 1500.
(a) 400 Seconds, Transformation Begins. (b) 500 Seconds, 25 Per Cent Transformed. (c) 850 Seconds, 50 Per Cent Transformed. (d) 900 Seconds, 75 Per Cent Transformed. (e) 2500 Seconds, 100 Per Cent Transformed.

which yields a better estimate of the beginning, progress and end of transformation, has recently been suggested by Austin and Rickett (59). The results of a series of observations at a sufficient number of temperature levels may be assembled on a single chart in which temperature of transformation is plotted vertically and time is plotted horizontally; smooth curves are drawn through the points represent-

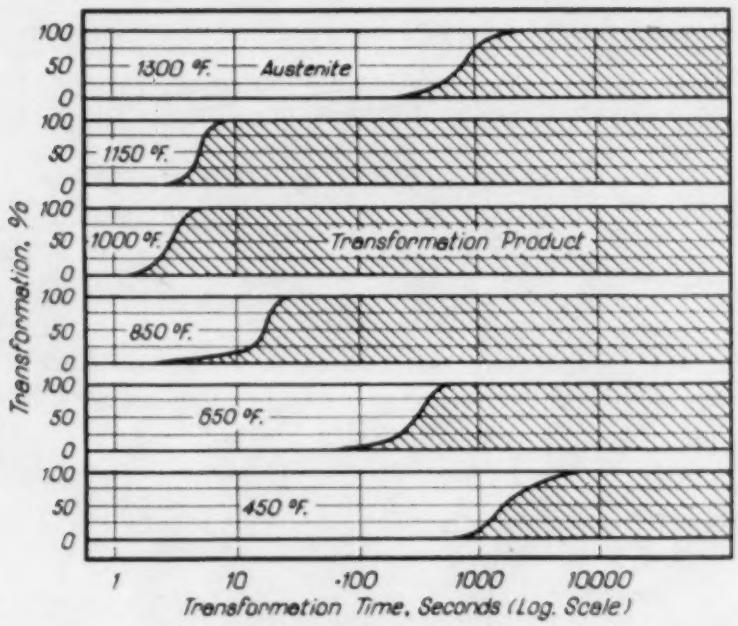


Fig. 5—Typical Curves Showing Progress of Transformation in a Single Steel at Five Different Temperature Levels. (Zimmerman, Aborn, Bain.)

ing the beginning and end of transformation at the different temperature levels and the result is the so-called "S-curve", a typical example of which is given in Fig. 6 taken from E. C. Bain's 1932 Campbell Lecture (9). Between the left-hand portion of the diagram representing austenite (black) and the right-hand portion representing transformation product (white) is a shaded band representing the time interval during which, at any given constant temperature, the transformation process is under way and in which it may be studied experimentally as outlined above.

Attention is called to two characteristic features of the S-curve: (a) the two temperature regions of relatively *rapid* transformation, one in the range 900 to 1100 degrees Fahr. (480 to 595 degrees Cent.) (the Ar′ region), the other at temperatures below about 200 degrees Fahr.; (b) the two temperature regions of relatively *slow* transformation, one just below the Ae_1 temperature, the other in the

temperature range 300 to 800 degrees Fahr. (150 to 425 degrees Cent.). These features of the curve are influenced by composition and grain size of the austenite and possibly by other factors, but the essential point is that these characteristic variations in speed of transformation at different temperature levels determine, to a large extent, the structure and properties obtained on cooling a given steel at a given rate from the austenitic range.

The upper region of rapid transformation in the vicinity of 900 to 1100 degrees Fahr. (480 to 595 degrees Cent.) has been variously

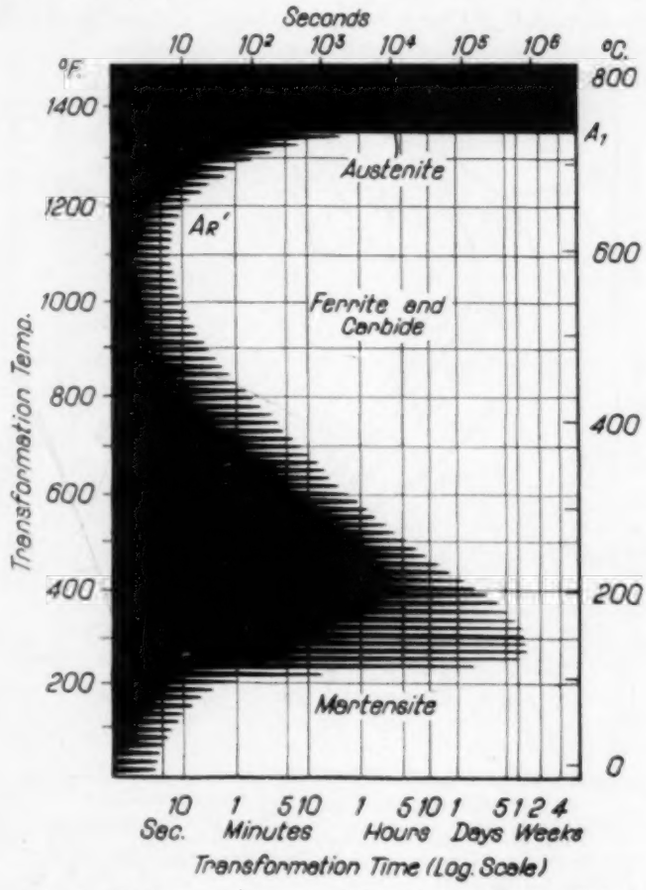


Fig. 6—Typical S-Curve for High Carbon Steel. (Bain.)

termed the "nose of the S-curve", "Ar′ region", "high temperature region of rapid transformation" and so on. Since this portion of the diagram must be mentioned repeatedly throughout the lecture, it will be called the "Ar′ range" merely as a matter of convenience in directing attention to this very important region of the curve. The logarithmic (or ratio) time scale is likewise merely a convenient means of including on a single diagram the extremely wide range

of time intervals encountered at the different temperature levels; on a linear scale for time, all detail for the shorter time intervals would be completely lost.

Sequence of Properties with Change of Transformation Temperature

The general relationship between the temperature of isothermal transformation and the resulting microstructure has been firmly established by thousands of observations on steels of relatively high carbon content (over 0.50 per cent carbon); this is shown schematically in Fig. 7. This general concept of the sequence of structures with change of transformation temperature is the basis of one point of view in the recent revival of interest in the question of proper metallographic nomenclature.

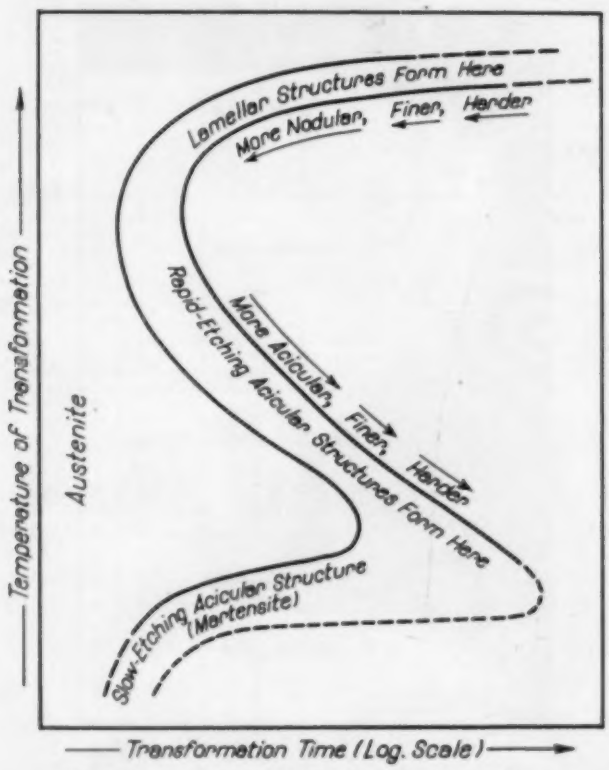


Fig. 7—Typical S-Curve with Ranges of Temperature for Formation of Lamellar and Acicular Products Indicated.

As would be expected, the mechanical properties of the products of isothermal transformation follow the trends of the microstructure; that is, as the transformation temperature decreases, the resulting structure becomes finer and finer and hardness and strength increase

while ductility decreases. As an example, the trend of hardness in some typical carbon and low alloy steels is shown in Fig. 8. There is, however, a temperature range, indicated by the shaded band, in which many steels fail to show the regular increase in hardness which might be expected from the corresponding decrease in transformation temperature. It is to be noted that this irregularity occurs in a temperature range corresponding approximately to the Ar′ range of the S-curve which, in turn, coincides with a marked change in the character of the transformation product. Within this particular

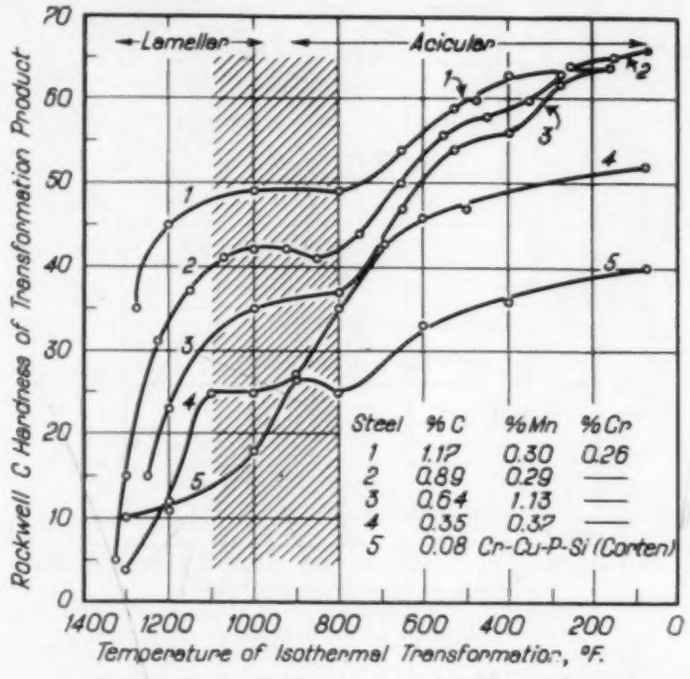


Fig. 8—Rockwell Hardness of Isothermal Transformation Products of Some Typical Carbon and Low-Alloy Steels.

range, 800 to 1100 degrees Fahr. (425 to 595 degrees Cent.), the microstructure changes from the lamellar or nodular to the acicular type; this is strongly suggestive of a fundamental change in the mode of transformation in this temperature range and there is ample evidence to support this view. A similar irregularity in the hardness curve occasionally appears in the *low* temperature range of rapid transformation, accompanying a change from the rapid-etching to the slow-etching acicular type of structure which, however, is not at all well-defined; further careful observations are needed to clarify this particular matter, and speculation seems beside the point until observations which can be interpreted unambiguously have been made.

The mechanical properties of the rapid-etching, acicular struc-

ture (bainite) resulting from isothermal transformation in the range 400 to 800 degrees Fahr. (205 to 425 degrees Cent.) have been investigated in some detail, and the results have shown consistently that this structure, particularly in carbon steels, possesses an unexpected degree of toughness and ductility at relatively high levels of

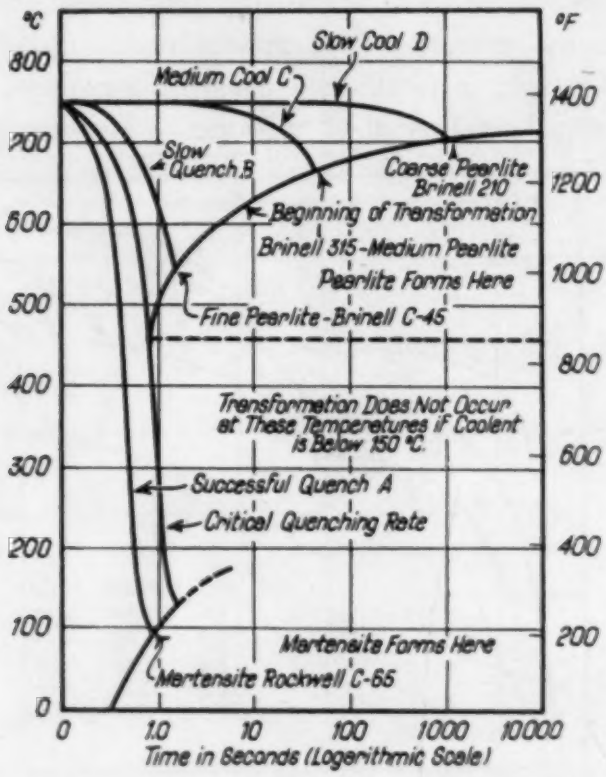


Fig. 9—Schematic Representation of Relation Between Cooling Rate and Temperature of Initial Transformation. (Bain.)

hardness (Rockwell C 50 to 60). Extensive investigation of these facts led eventually to the development of a new method of heat treatment based upon isothermal transformation in this temperature range; this process is now commonly known as "austempering" (41), (42), (69), (70), (71).

Isothermal and Cooling Transformation Diagrams

In 1932 Bain (9) published a diagram, reproduced in Fig. 9, which shows schematically the essential relationship between cooling rate and the isothermal S-curve. It is obvious that we can obtain a transformation diagram based upon different speeds of cooling from above the transformation range, and that this might be designated the "cooling transformation curve" as contrasted to the "isothermal

transformation curve" with which we are at present on more familiar terms. Such a "cooling transformation curve" would be generally similar in shape to the "isothermal S-curve", except that, as Bain pointed out, the portion just below or "sheltered" by the Ar′ region would be missing. Experimental evidence now indicates quite definitely that the cooling transformation curve lies below and to the right of the isothermal S-curve, as would be expected; the exact relationship between the two types of diagram is far from simple (63), (73) and further experimental work is needed for its complete clarification; such investigations have been actively under way for some time at the laboratory with which the author is connected. Moreover, in any consideration of this aspect of the subject, it must be borne in mind that continuous cooling treatments tend to give rise to a *range* or *series* of structures corresponding to the range of temperature over which the transformation may take place, as contrasted to isothermal treatments which, as it turns out, produce a *uniform* structure characteristic of the particular temperature level involved. It will presently be seen that this is a matter of considerable importance in some of the slow-transforming alloy steels.

Significance of Isothermal Transformation Investigations

After approximately ten years of experience in this field it appears that the investigations of isothermal transformation have contributed to an improved understanding of the heat treatment of steel in at least four major ways:

1. They have provided us with a new, more comprehensive and clearer picture of the transformation of austenite, which in turn furnishes a new basis for a broad, general philosophy of heat treatment. By learning to *think* in terms of the S-curve, one finds that many facts, long recognized but only vaguely correlated, fall into proper place in a consistent picture of the whole subject of heat treatment.

2. They have demonstrated the outstanding influence of the actual temperature of transformation on the character and properties of the several structures possible in a given steel, and on the essentially continuous variation producible in any single category of structures, such as the lamellar series (pearlite), or the acicular series (bainite or martensite).

3. They have permitted us to evaluate the influence of alloying

elements on microstructure, mechanical properties, depth of hardening, and on many other criteria employed to judge the results of heat treatment. Chemical composition of the austenite, prior to cooling, profoundly influences the shape and location of the S-curve, hence the response to a given heat treatment; and it is in this field that isothermal transformation studies are of practical value in enabling us to account for the specific effects produced by an element or combination of elements in solution in the austenite.

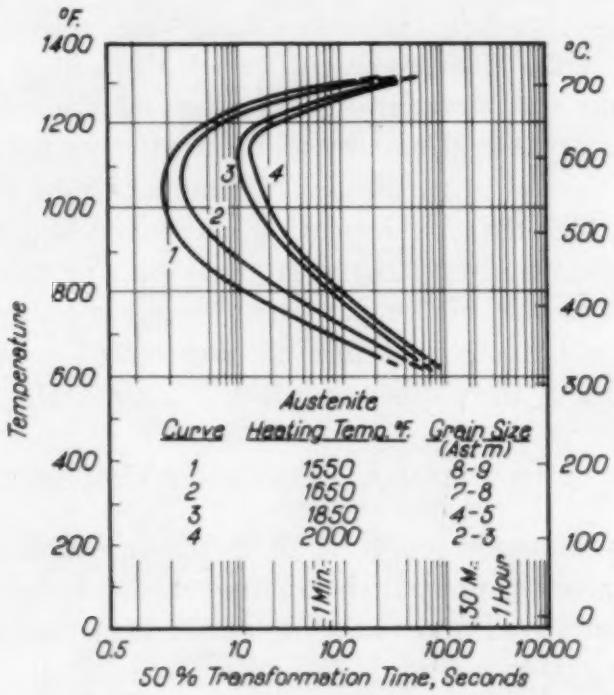


Fig. 10—Comparative Time Intervals for 50 Per Cent Transformation in a Single Steel as Influenced by Austenite Grain Size.

4. They have contributed to a rational explanation of the influence of coarser austenite grain size, which displaces the S-curve in much the same manner as an alloying element. A typical example of the effect of austenite grain size on the location of the S-curve of a high carbon steel is shown in Fig. 10; as the grain size increases, the Ar′ region of the S-curve moves significantly to the right reflecting the increased reluctance of the steel to transform. This accounts for the long-recognized fact that higher heating temperatures, which produce coarser austenite grains, give rise to deeper hardening.

In brief, then, the isothermal transformation rate is fundamental, and any factor or set of circumstances which influences it, and thus

affects the shape and location of the S-curve, will exert a corresponding influence on the response of the steel to heat treatment.

Influence of Alloying Elements

In covering this aspect of the subject I shall first discuss the influence of certain individual elements—carbon, manganese, nickel, chromium, molybdenum, vanadium and cobalt—as revealed by isothermal transformation studies. In view of the fact that the results of approximately ten years' work are being summarized here, much more could be said than is possible in a single lecture; in any case, it is our belief that the essential trends are adequately revealed by the curves themselves and that extended comment would be superfluous. Insofar as possible, the influence of each element will be demonstrated by means of comparison charts which show how the S-curve is modified in shape and position as the amount of the element under consideration increases. In order to avoid a confusing multiplicity of curves on comparison charts for *hypoeutectoid* steels, we have arbitrarily omitted the curve for beginning of proeutectoid ferrite separation at the higher temperature levels (Ar′ range and above) and have shown only the curves for beginning of formation of lamellar products (pearlite), since we believe the pearlite curve is more significant from the standpoint of heat treating practice; the curve for beginning of ferrite separation would, of course, lie to the left of the upper portion of the S-curve.

In these comparisons, austenite grain size, incidental elements, degree of solution of carbides and other factors which might influence the trends, were either held constant or maintained within narrow limits. The comparison charts show the curves for both beginning (left) and ending (right) of transformation; both curves are shown because, in many instances, the characteristic trend imparted by the alloying element under consideration is revealed more clearly by one than the other; in a few instances the curve for 50 per cent transformation is shown instead of the beginning and ending curves. In many cases only the portion in the vicinity of the Ar′ range is shown since this is the most significant part of the curve with respect to ordinary heat treating operations. Following the discussion of the effect of individual alloying elements, there will be presented the isothermal transformation curves of a number of alloy steels of the S.A.E. series (0.35 to 0.45 per cent carbon grade); the S.A.E.

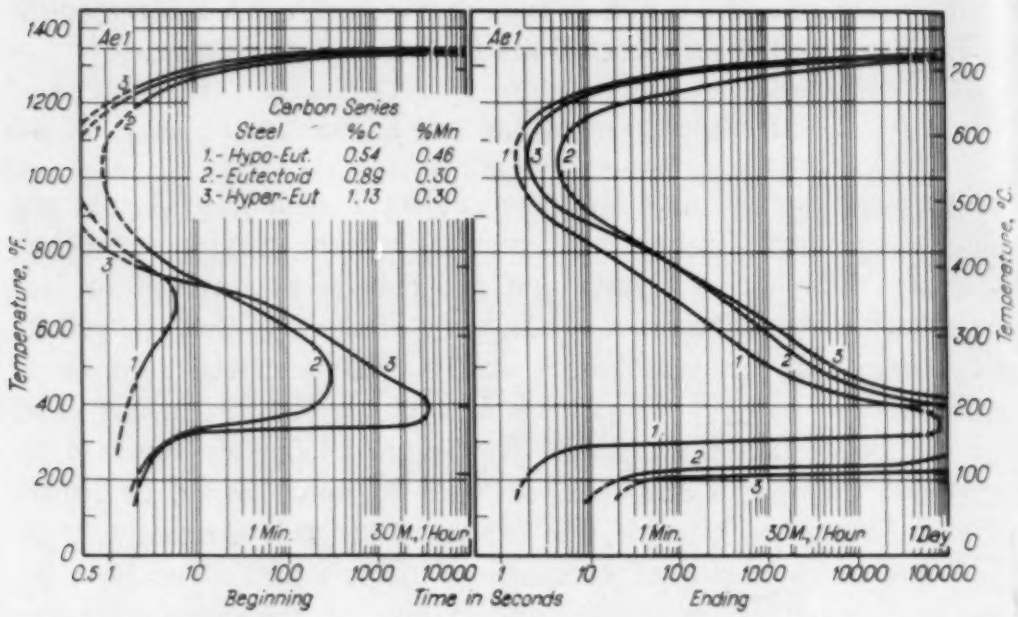


Fig. 11—Comparison Chart Showing Influence of Carbon on the Isothermal Transformation Curve. Left, Beginning Curves; Right, Ending Curves.

steels investigated include some of the more popular and widely used compositions.

The equilibrium transformation temperatures, Ae_1 and Ae_3, shown on many of these diagrams were determined by means of metallographic observations and hardness tests on series of specimens brine quenched from temperatures in the vicinity of the A_1 and A_3 points after holding for a period sufficiently long to obtain substantial equilibrium.

Influence of Individual Elements

Carbon—Fig. 11 shows the influence of carbon content as revealed by the S-curves of three steels containing 0.54, 0.89 and 1.13 per cent carbon respectively, all with manganese in the range 0.30 to 0.45 per cent. These curves indicate that the hypereutectoid steel (1.13 per cent carbon) is the fastest of the three to start transforming in the Ar′ range; this behavior has been observed repeatedly and is probably associated with the rejection of proeutectoid carbide ahead of the formation of pearlite, these carbide particles then serving as nuclei which speed up the pearlite reaction. The curves for the hypoeutectoid and eutectoid steels are in the same relation to each other in the Ar′ range as they are at lower temperature levels where the transformation is markedly and consistently retarded with in-

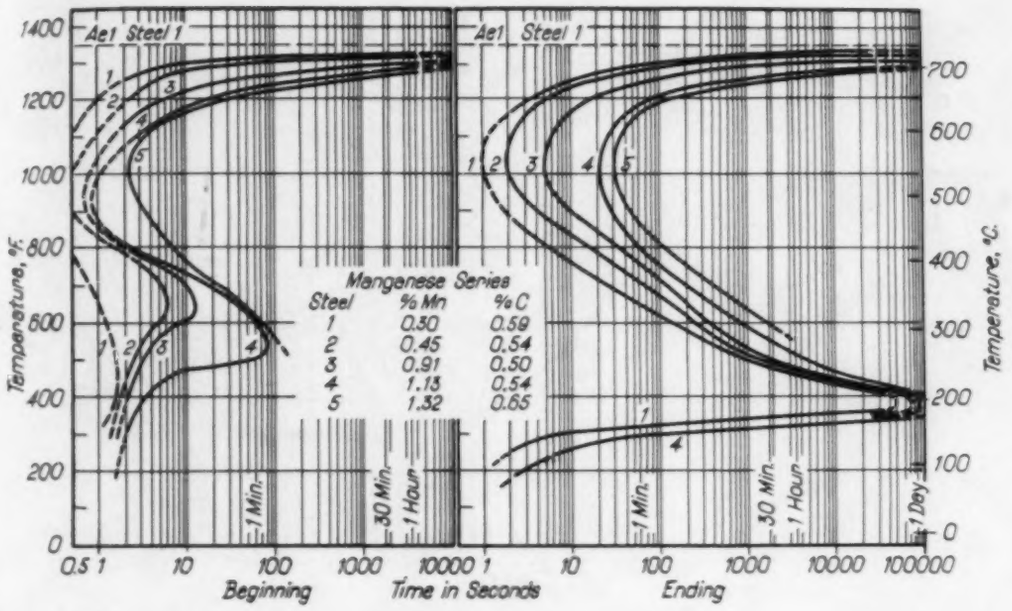


Fig. 12—Comparison Chart Showing Influence of Manganese on the Isothermal Transformation Curve. Left, Beginning Curves; Right, Ending Curves.

creasing carbon content. Attention is called to the fact that the low-carbon member of the series (0.54 per cent carbon) begins to transform quite rapidly in the intermediate temperature range (400 to 700 degrees Fahr.), in which range the higher carbon steels behave very sluggishly; this effect will be even more evident when we come to the discussion of the 0.35 to 0.45 per cent carbon steels of the alloy series.

Manganese—The influence of manganese as revealed in a series of steels containing 0.50 to 0.65 per cent carbon is shown in Fig. 12. The general effect of this element is to retard the transformation at all temperature levels; indeed, Bain (8) showed that when the manganese content reaches some 6 to 7 per cent the transformation is so very slow that it requires about four weeks to go to completion at 975 degrees Fahr. (525 degrees Cent.). Thus, through a knowledge of the transformation rates involved, we have at hand a logical explanation of the long-known and well-established fact that manganese is an effective element for increasing depth of hardening.

Nickel—The influence of nickel in a series of steels containing 0.50 to 0.60 per cent carbon is shown in Fig. 13. Nickel, like manganese, is an element which consistently retards the transformation at all temperature levels, but much less markedly than manganese, as shown by Bain (8) and as can be readily seen from a comparison of Figs. 12 and 13. Since a fairly high percentage of nickel is pres-

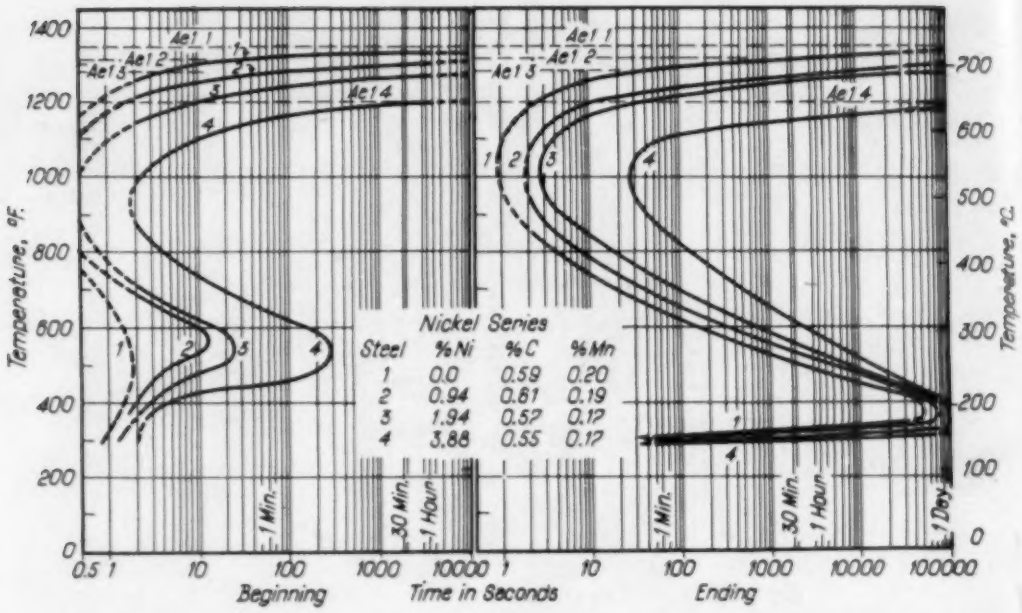


Fig. 13—Comparison Chart Showing Influence of Nickel on the Isothermal Transformation Curve. Left, Beginning Curves; Right, Ending Curves.

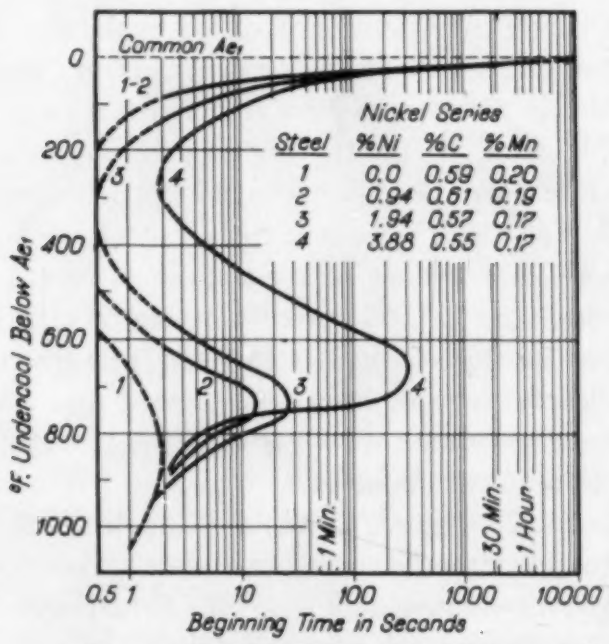


Fig. 14—Beginning Curves of Fig. 13 with "Degrees Undercool Below Ae_1" Plotted Vertically Instead of the Usual Temperature Scale.

ent in some of these steels, and since nickel is an element which lowers the Ae_1 temperature, it may be of interest to compare the curves when plotted on a temperature scale expressed in terms of the "degree of undercool below Ae_1" instead of the usual temperature

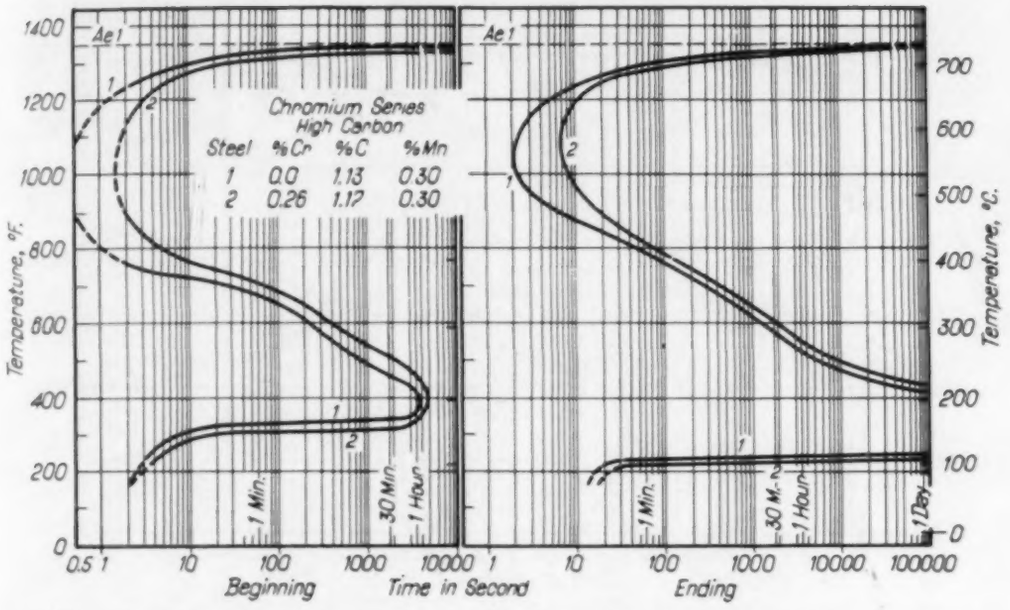


Fig. 15—Comparison Chart Showing Influence of Chromium on the Isothermal Transformation Curve of High Carbon Steel. Left, Beginning Curves; Right, Ending Curves.

scale. In effect, this method of plotting gives all the curves a common Ae_1 line and serves to eliminate possible confusion arising from the lowering of the Ae_1 and the resultant "squashing down" of the S-curve itself with increasing nickel content. The curves for beginning of transformation are shown plotted on this basis in Fig. 14, and it is obvious that no particularly significant relationships are brought to light by this method of plotting; it is interesting to note, however, that the Ar′ range of the 3.88 per cent nickel steel appears to be definitely lifted to a higher temperature level, relative to Ae_1, as compared to the three other steels.

Chromium—The influence of a small amount of chromium in high carbon steel is shown in Fig. 15; this element appears to be more effective in retarding the transformation in the Ar′ range than manganese, which itself is more effective than either carbon or nickel.

The influence of chromium in a series of steels containing 0.32 to 0.42 per cent carbon is shown in Fig. 16. In these lower carbon steels chromium is revealed as a very effective element for retarding the transformation in the Ar′ range, thus furnishing a rational explanation of the marked air-hardening tendencies of many of the chromium-bearing steels. Note, particularly, the characteristic form imparted by chromium to the upper portion of the curves, and how this effect increases in intensity with increasing chromium content.

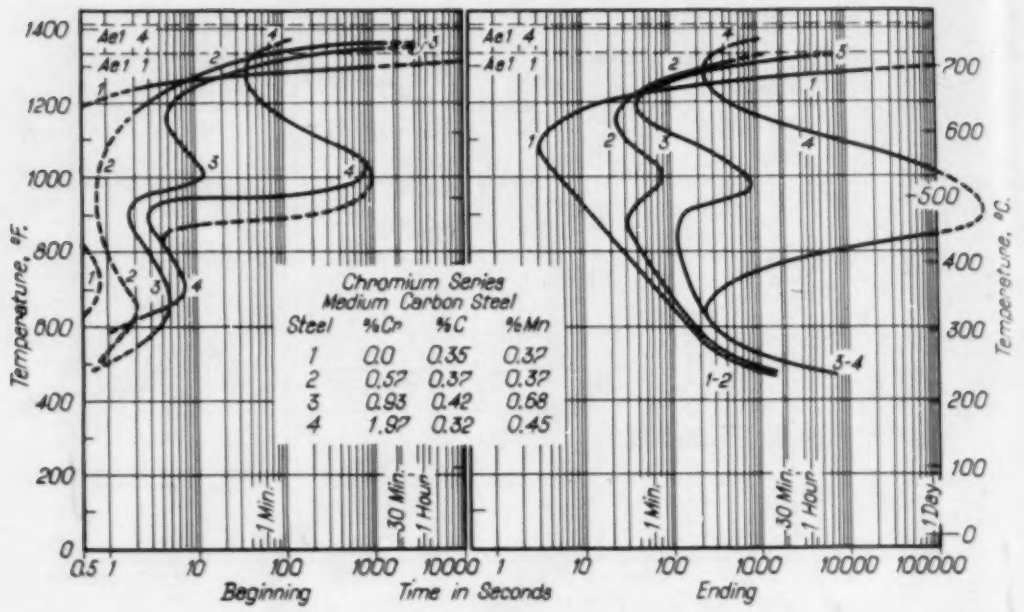


Fig. 16—Comparison Chart Showing Influence of Chromium on the Isothermal Transformation Curve of Medium Carbon Steel. Left, Beginning Curves; Right, Ending Curves.

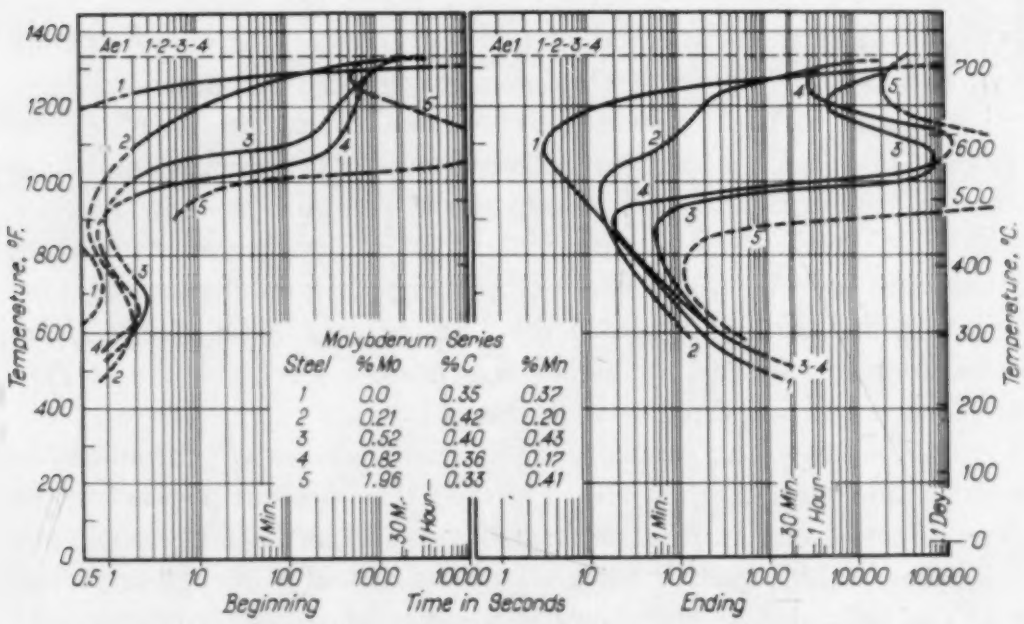


Fig. 17—Comparison Chart Showing Influence of Molybdenum on the Isothermal Transformation Curve. Left, Beginning Curves; Right, Ending Curves.

The broken line in the curve for the 2 per cent chromium steel represents what we believe to be the beginning of a second stage of transformation in this range of temperature; this point will be discussed in further detail in a subsequent section. Note how the lower carbon content of these steels is reflected in the form of the beginning curve

at the lower temperature levels, indicating that carbon is the element which largely determines the form and location of this portion of the beginning curve. The rather surprising effects of alloying elements, as revealed by isothermal transformation diagrams such as those for the chromium steels (Fig. 16), will become increasingly evident as the story continues, particularly when the S.A.E. steels are taken up for discussion.

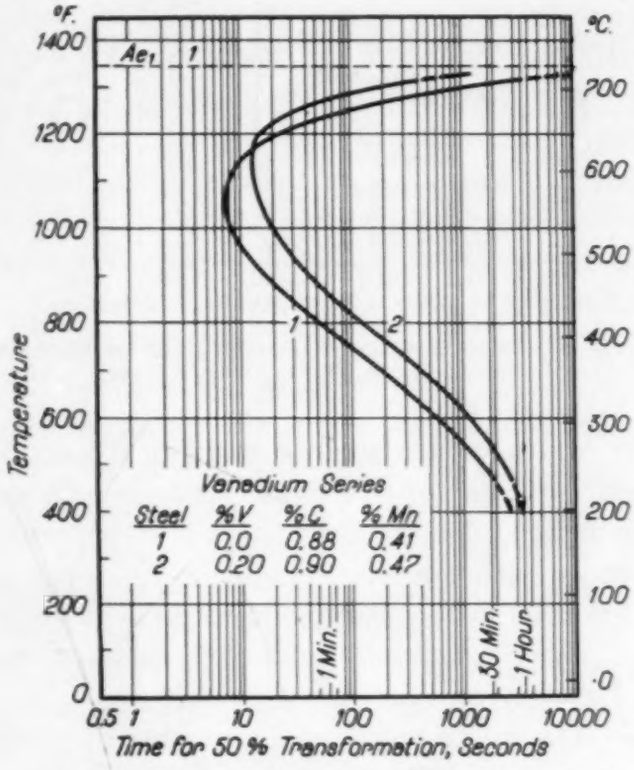


Fig. 18—Comparison Chart Showing Influence of Vanadium on the Isothermal Transformation Curve of High Carbon Steel. (Zimmerman, Aborn, Bain.) These Curves Represent the Time Required for 50 Per Cent Transformation, Instead of the Beginning or Ending Time as Shown in Previous Comparison Charts.

Molybdenum—Fig. 17 illustrates the influence of molybdenum as shown by the curves for a series of steels containing 0.35 to 0.42 per cent carbon. Like chromium, molybdenum imparts a peculiar and characteristic form to the upper portion of the isothermal transformation curve, and up to about 0.5 per cent appears to be much more effective than chromium in retarding the transformation at temperatures above 1000 degrees Fahr. (540 degrees Cent.). It appears that between 0.5 and 0.8 per cent molybdenum there is little or no significant change in the shape of the curve; the minor inconsistencies

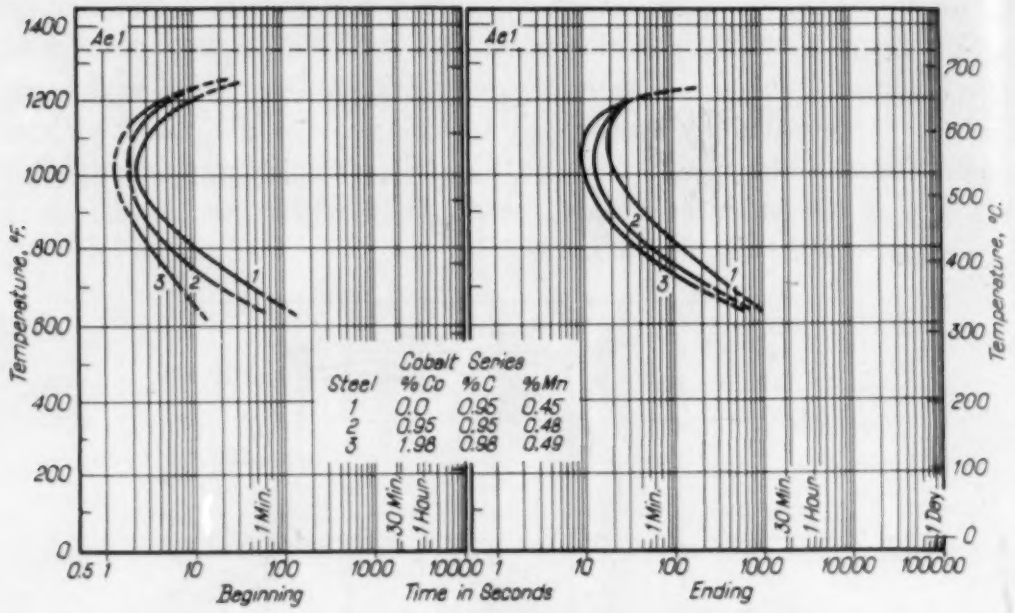


Fig. 19—Comparison Chart Showing Influence of Cobalt on the Isothermal Transformation Curve. Left, Beginning Curves; Right, Ending Curves.

observed in the curves for the steels containing 0.5 and 0.8 per cent molybdenum may well be due to the difference in manganese content of these two materials. An attempt was made to determine the curve for a 2 per cent molybdenum steel containing 0.33 per cent carbon; the structures revealed in this steel were so difficult to interpret that we consider the curve to be only tentatively worked out, and it is shown in Fig. 17 solely on this basis.

Vanadium—The influence of small amounts of vanadium (0.20 to 0.30 per cent) on the transformation rate of high carbon steel has been investigated quite thoroughly and reported upon elsewhere (39). Fig. 18 shows the S-curve (50 per cent transformation) of a vanadium steel, with the vanadium actually in solid solution in the austenite, as compared to that of a comparable vanadium-free steel; it is seen that vanadium retards the transformation at and below the Ar′ range, but at higher temperature levels it appears to accelerate it.

Cobalt—Cobalt has been reported to be an element which promotes shallow hardening (7), (9), (58). Since this alleged influence of cobalt appeared to be at variance with the effect of other alloying elements in steel, it seemed desirable to investigate the question by the isothermal transformation technique. Accordingly, a series of high carbon steels (0.95 per cent carbon) was prepared, containing 0, 1 and 2 per cent cobalt and the portion of the S-curve

between 700 and 1200 degrees Fahr. (370 and 650 degrees Cent.) was determined for each. The results are shown in Fig. 19 which indicates quite clearly that cobalt actually accelerates the transformation of austenite in the Ar′ range. There is no ready explanation for what appears to be the unique influence of this element, although it has been suggested that it may be related in some way to the fact that cobalt undergoes an allotropic transformation of its own, in a temperature range not far from that in which iron transforms.

So much for the influence of individual alloying elements. It appears that, with the exception of cobalt, almost any element which can be put into true solid solution in austenite retards the transformation of that austenite when cooled below its temperature range of stable existence; in other words, alloying elements (cobalt excepted) move the S-curve to the right on the time axis. Thus, for a given rate of cooling of austenite, the alloy steel transforms at lower temperatures and hence forms harder, stronger structures than does a carbon steel comparably treated. Stating it somewhat differently, the alloy steels are deeper hardening than carbon steels because they have S-curves which lie farther to the right and hence have slower so-called "critical cooling rates". However, many of the alloying elements form carbides, oxides or other compounds which are relatively reluctant to go into solution in austenite, and unless real solid solution is achieved, the *apparent* influence of a particular element may be quite different from that outlined above; conversely, with a little experience, the isothermal transformation rate, at some significant temperature level, conceivably may be used as a rough indication of whether or not the alloying elements present are in true solution in the austenite.

Isothermal Transformation Curves of S.A.E. Alloy Steels

Turning now to the influence of alloying elements as revealed by the isothermal transformation curves of some typical, commercial S.A.E. alloy steels of the 0.35 to 0.45 per cent carbon grade, let us first consider the diagrams for the individual steels. The curves were determined both by the metallographic and dilatometric methods at about 100 degrees Fahr. intervals down to 400 to 500 degrees Fahr. (205 to 260 degrees Cent.); within the limits of experimental error, the results obtained by the two methods checked remarkably well.

The list of steels investigated is shown in Table I, together with

the chemical analysis, heating (austenitizing) temperature used, austenite grain size obtained at that temperature, and other pertinent data. In general, a heating temperature comparable with that used in commercial practice was employed in working out the isothermal transformation diagrams of these steels; this was done in order that

Table I
Data on S.A.E. Steels Investigated

Steel S.A.E. No.	Chemical Composition, Per Cent							Equilibrium Transformation Temperatures		Austenite		
	C	Mn	Si	Ni	Cr	Mo	V	Ae_1 (°F)	Ae_3 (°F)	Heating Temp. (°F)	Time (Mins.)	Grain Size (ASTM)
2340	0.37	0.68	0.21	3.41	....	....	....	1225	1350	1450	15	7-8
T-1335	0.35	1.85	0.19	....	....	....	....	1295	1430	1550	15	70% 7 + 30% 2
5140	0.42	0.68	0.16	0.07	0.93	....	....	1360	1425	1550	15	6-7
3140	0.38	0.72	0.21	1.32	0.49	....	....	1305	1390	1550	15	7-8
4140	0.37	0.77	0.15	0.04	0.98	0.21	....	1365	1445	1550	15	7-8
6140	0.43	0.74	0.23	0.06	0.92	....	0.16	1365	1440	1550	15	8
4640	0.36	0.63	0.19	1.84	0.06	0.23	....	1280	1395	1550	15	7-8
4340	0.42	0.78	0.24	1.79	0.80	0.33	....	1300	1375	1550	15	7-8
5 Cr-Mo	0.11	0.38	0.44	0.15	5.46	0.42	....	1475	1535	1650	15	7-8

the data obtained might be as practically useful as possible, even though, in some instances, it meant that the full alloy content of the steel was not in solid solution in the austenite. All the steels were given a preliminary normalizing treatment consisting of air-cooling from 1800 degrees Fahr. (980 degrees Cent.) in the form of 1 to 1⅜-inch rounds.

The isothermal transformation curves are shown in Figs. 20 to 28 inclusive and since these diagrams, in a sense, tell their own story more eloquently than any words could, only brief comment will be made on the more important features of the curves in each individual case. Full appreciation of the peculiarities of these S.A.E. steel curves can best be had by frequent comparison with the eutectoid steel S-curve (Fig. 6) and with those showing the influence of individual alloying elements presented earlier (Figs. 11 to 19). Since, in this group, only a single steel is dealt with on each chart, it has been possible to show the line for beginning of proeutectoid ferrite rejection, as well as the line for beginning of formation of lamellar product, at the higher temperature levels; thus the relationship of these two lines to the Ae_3 and Ae_1 temperatures, respectively, is clearly brought out. The Rockwell C hardness obtained after complete transformation at the different temperature levels is also indicated on each diagram.

As the discussion of the S.A.E. steel curves proceeds, it may be

helpful to regard the diagram as a kind of map, in which the region between beginning and end of transformation to the "ferrite-carbide" aggregate corresponds to land, and the regions on either side to water; thus the water on the left would be the "austenite sea" and that on the right the "ferrite plus carbide sea". Following out this simile, we shall have occasion to refer to "bays" and "promontories"

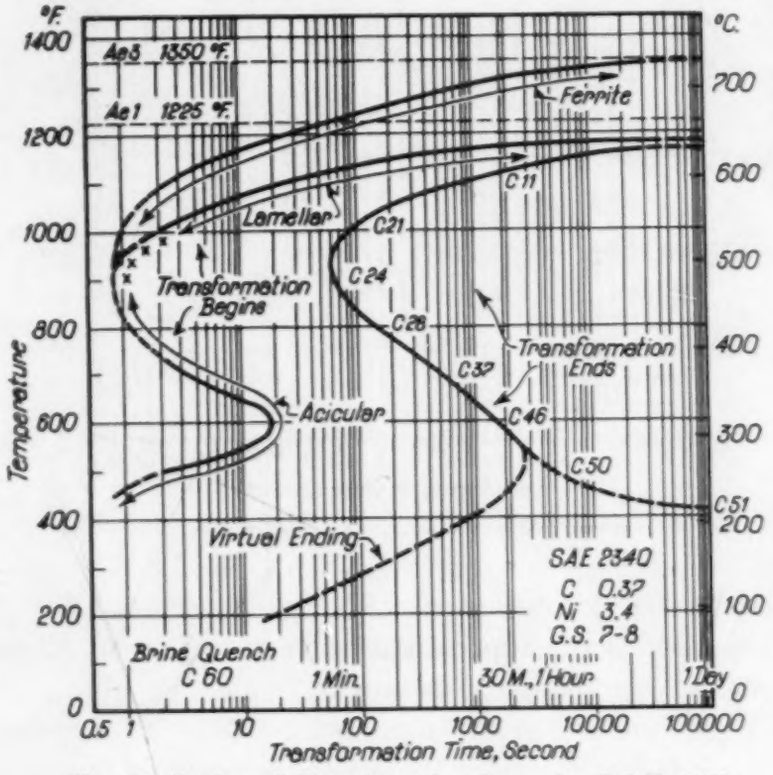


Fig. 20—Isothermal Transformation Curve for S.A.E. 2340.

in discussing some of the peculiar features of these rather strange-looking curves. The series of X's appearing between the ranges for lamellar and acicular products of transformation represents an intermediate type of structure which will be discussed in a subsequent section of the lecture. Attention is also directed to a convention used for representing the end of transformation at the lower temperature levels, 500 to 600 degrees Fahr. (260 to 315 degrees Cent.) and below; the curve labelled "Transformation Ends" represents, as well as could be determined experimentally, what we believe to be the true (100 per cent) end of transformation at these temperatures; note that this line extends out to extremely long time periods, an observation which is consistent with the well-known tendency of many of these alloy steels to retain some proportion of austenite per-

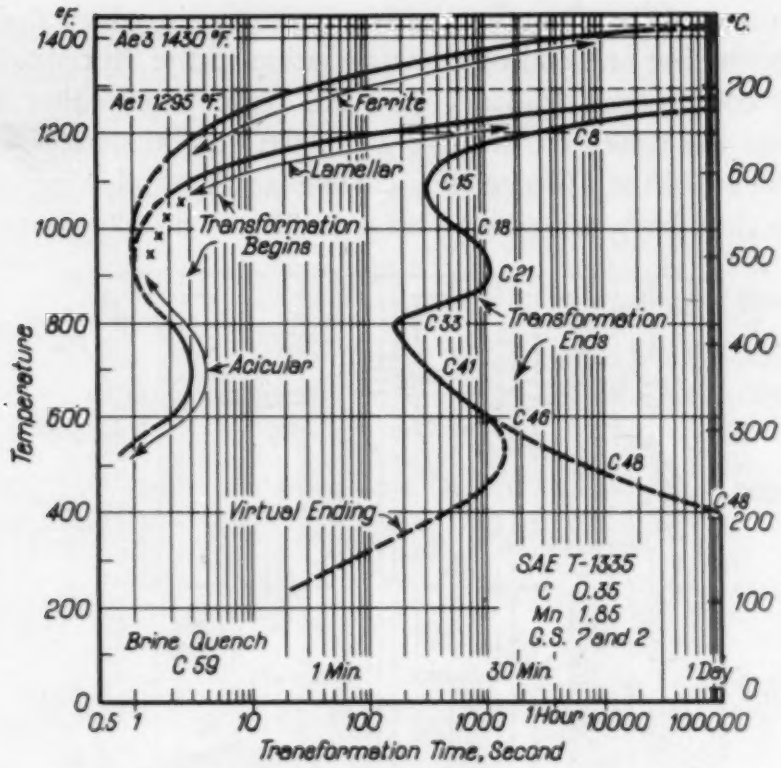


Fig. 21—Isothermal Transformation Curve for S.A.E. T-1335.

manently at room temperature. Another curve, labelled "Virtual Ending", represents the approximate time for the transformation to go to substantial completion; this time is, in most instances, of greater practical significance than the time for complete transformation of every last trace of austenite at these low temperature levels.

S.A.E. 2340 (3.25 to 3.75 Per Cent Nickel)—This curve (Fig. 20) has the same characteristic "S" shape as the curves for plain carbon steels of higher carbon content; however, the interval between beginning and ending lines is relatively wide; and the influence of the relatively low carbon content is evident in the manner in which the line for beginning of transformation at the lower temperature levels is pushed toward the left as compared to the same line in the diagrams for higher carbon steels. This influence of carbon on the lower portion of the S-curve was mentioned earlier, and the same general effect may be noted in the curves for all of the S.A.E. steels examined. The whole curve for S.A.E. 2340 has a "squashed down" appearance due, of course, to the lowering of the Ae_1 and Ae_3 temperatures by the relatively large amount of nickel present in this steel.

S.A.E. T-1335 (1.60 to 1.90 Per Cent Manganese)—The diagram for this steel (Fig. 21) shows the extremely wide time interval between beginning and ending lines and the increased reluctance of the transformation to go to completion at temperatures in the vicinity of 900 degrees Fahr. (480 degrees Cent.). Thus we have a "promontory" in the ending line, and it will presently become evident that

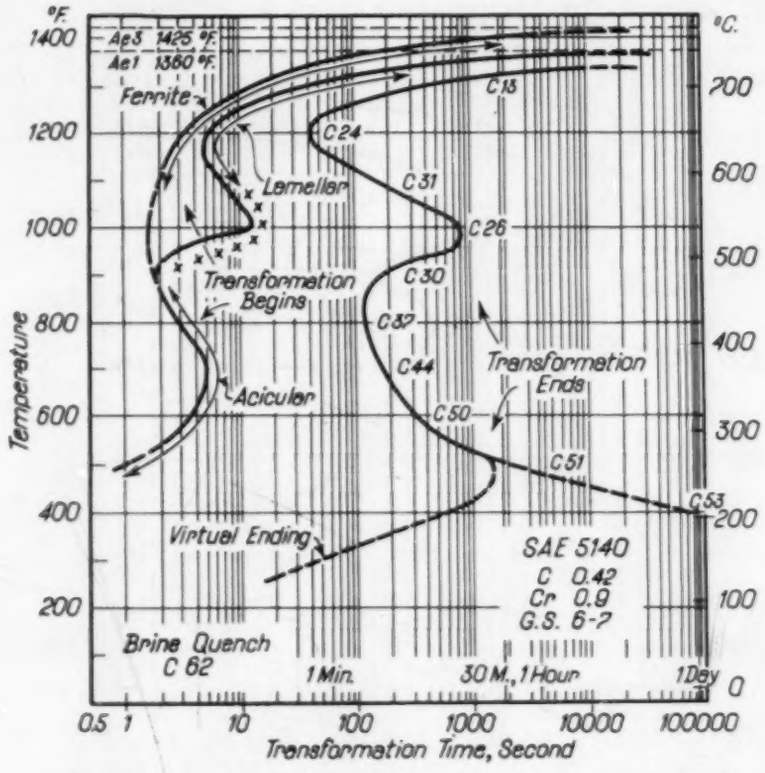


Fig. 22—Isothermal Transformation Curve for S.A.E. 5140.

this feature is characteristic of all these alloy steels which contain appreciable amounts of carbide-forming elements. The promontory effect may be clearly seen in the comparison chart for the straight chromium steels (Fig. 16) as well as in that for the molybdenum series (Fig. 17); moreover, if the alloying element is a strong carbide-former such as chromium or molybdenum, the beginning line takes on the characteristic form of the ending line, thus giving rise to a "bay", as the alloying element is increased in amount. Indeed, this seems to be one of the outstanding effects contributed by the alloying elements occurring in the S.A.E. steels investigated, and this feature will be referred to several times in the following discussion.

S.A.E. 5140 (0.80 to 1.10 Per Cent Chromium)—The curve for this steel (Fig. 22) indicates that this amount of chromium is suffi-

cient to modify the shape of the beginning curve as well as the ending curve, thus resulting in a bay in the vicinity of 1000 degrees Fahr. (540 degrees Cent.). Note that the curve for beginning of ferrite rejection is not greatly altered as compared to steels without chromium (S.A.E. 2340 and T-1335), although the whole S.A.E. 5140 curve is stretched vertically due to the action of chromium in raising the Ae_1 and Ae_3 temperatures.

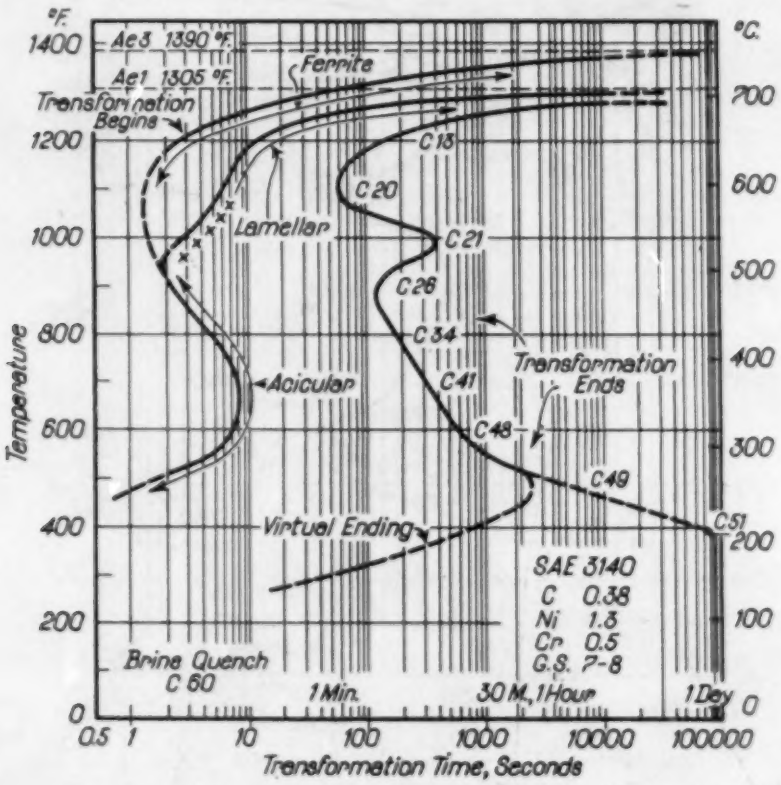


Fig. 23—Isothermal Transformation Curve for S.A.E. 3140.

S.A.E. 3140 (1.00 to 1.50 Per Cent Nickel; 0.45 to 0.75 Per Cent Chromium)—Fig. 23 shows the curve for this steel and it is seen that while the small amount of chromium involved here is sufficient to modify the ending curve, it just barely makes itself evident in the beginning curve and practically not at all in the ferrite curve.

S.A.E. 4140 (0.80 to 1.10 Per Cent Chromium; 0.15 to 0.25 Per Cent Molybdenum)—This curve (Fig. 24), as compared to the curve for S.A.E. 5140 of similar chromium content, shows that this combination of chromium and molybdenum results in a pronounced alteration in the shape and location of both the beginning and ending curves at the higher temperature levels. It is to be noted that this steel is the most sluggish in its isothermal transformation behavior

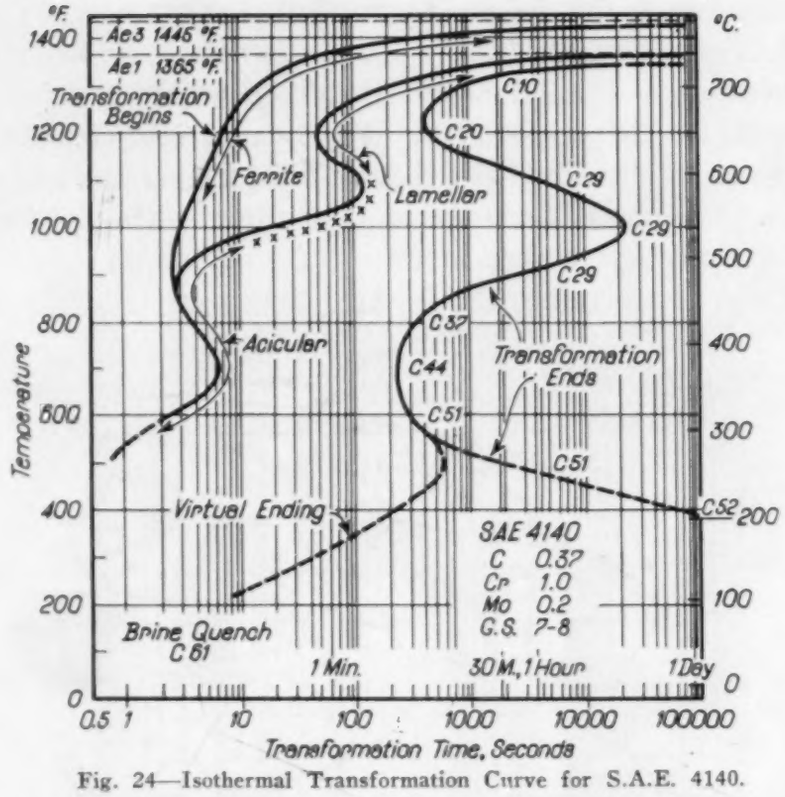


Fig. 24—Isothermal Transformation Curve for S.A.E. 4140.

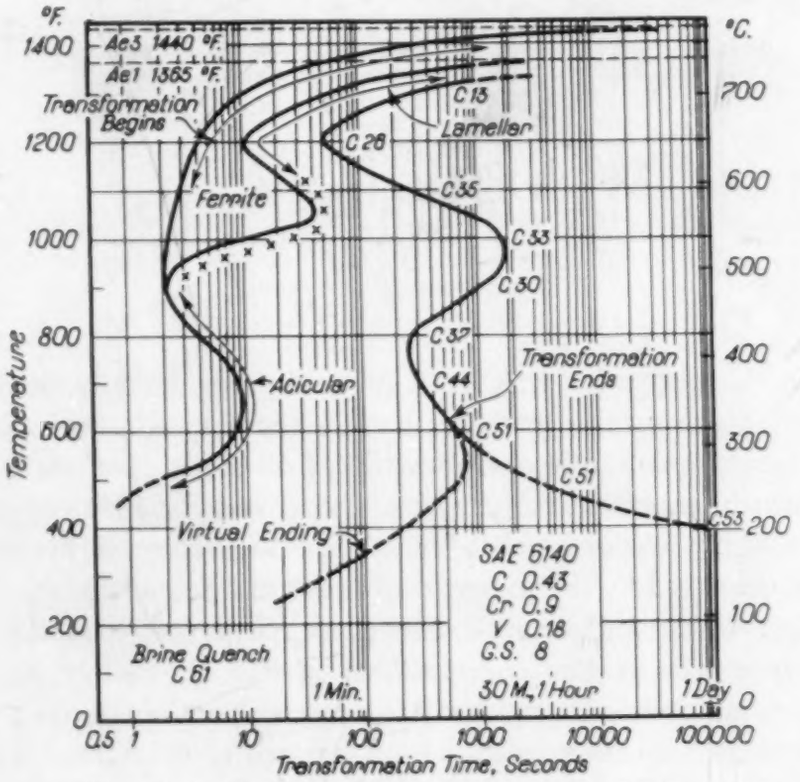


Fig. 25—Isothermal Transformation Curve for S.A.E. 6140.

of any of the steels that have yet been discussed in the S.A.E. series.

S.A.E. 6140 (0.80 to 1.10 Per Cent Chromium; 0.15 to 0.18 Per Cent Vanadium)—Fig. 25 shows that the curve for this steel is quite similar to that for S.A.E. 5140, both steels containing the same amount of chromium but S.A.E. 6140 having the addition of vanadium. The upper bay in the beginning line is lifted to a slightly higher temperature level than in the straight chromium steel (S.A.E. 5140); this effect may also be detected, to an even slightly greater

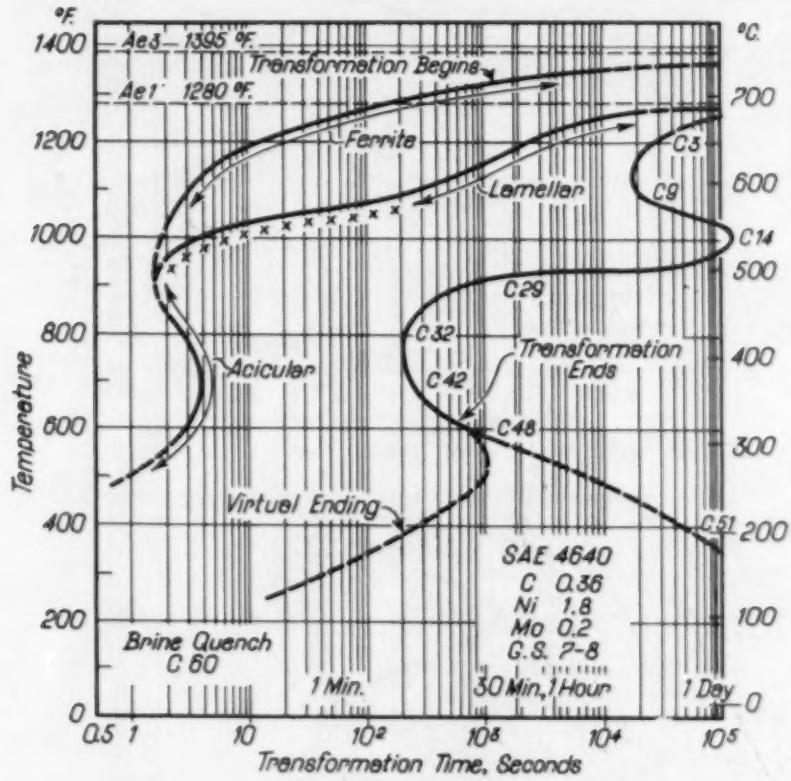


Fig. 26—Isothermal Transformation Curve for S.A.E. 4640.

extent, in the curve for S.A.E. 4140 steel. Incidentally, it should be evident by this time that this bay in the line for beginning of lamellar transformation is characteristic of all steels containing chromium much in excess of 0.5 per cent; moreover, the intensity of the effect is roughly proportional to the chromium content, although it is obviously enhanced by the presence of other alloying elements.

S.A.E. 4640 (1.65 to 2.00 Per Cent Nickel; 0.20 to 0.30 Per Cent Molybdenum)—The curve shown in Fig. 26 clearly indicates the tremendous influence exerted by this combination of nickel and molybdenum. Note the exceedingly protracted time interval between the beginning and end of transformation in the range 950 to 1200

degrees Fahr. (510 to 650 degrees Cent.). Attention is called to the fact that, in the absence of chromium, the upper bay in the beginning line is practically nonexistent and is replaced, instead, by a roughly horizontal portion, or "shelf", in the vicinity of 1050 to 1100 degrees Fahr. (565 to 595 degrees Cent.). This "shelf" is clearly evident in the beginning curves for the straight molybdenum steels (Fig. 17),

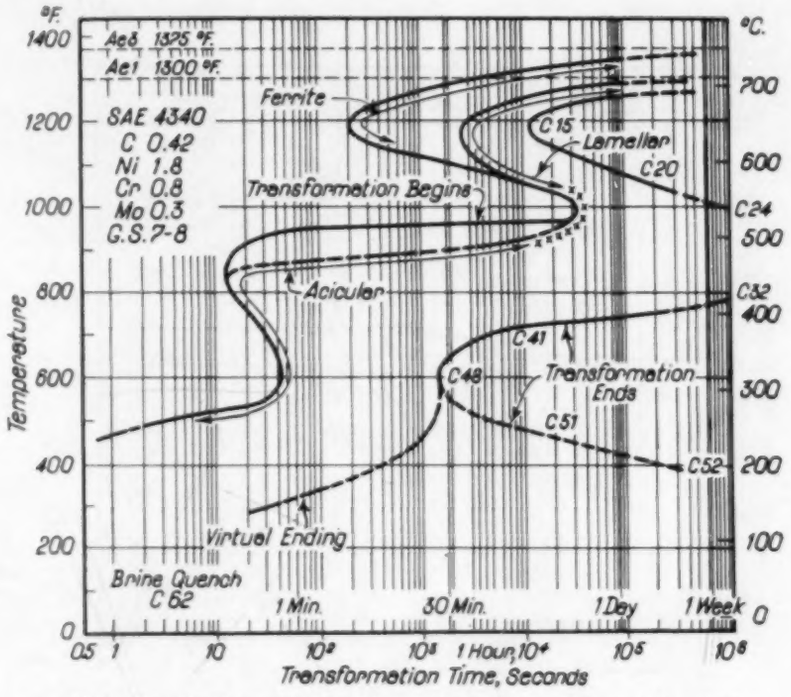


Fig. 27—Isothermal Transformation Curve for S.A.E. 4340.

but it is interesting to note that when the molybdenum content reaches about 2 per cent, this element also gives rise to the formation of a bay in the beginning curve, in much the same manner as chromium.

S.A.E. 4340 (1.50 to 2.00 Per Cent Nickel; 0.50 to 0.80 Per Cent Chromium; 0.30 to 0.40 Per Cent Molybdenum)—Fig. 27 shows the isothermal transformation curve obtained when all three elements, nickel, chromium and molybdenum, are present in the steel. The extremely sluggish behavior of this steel at the higher temperature levels is, of course, reflected in the characteristic high hardenability of steels of this general composition. Note that this is the first of the S.A.E. steels in which the ferrite line definitely turns in to the right and follows the contour of the bay in the beginning line; in fact, the two lines merge at about 1050 degrees Fahr. (565 degrees Cent.) and ferrite, as a definite constituent, does not again appear in this steel at lower temperature levels. Attention is directed

to the extremely long time interval for completion of transformation in the range 750 to 1050 degrees Fahr. (400 to 565 degrees Cent.); for example, after 17 days at 900 degrees Fahr. (480 degrees Cent.) the transformation was only about 40 per cent completed. The pronounced shelf at 950 degrees Fahr. (510 degrees Cent.) is undoubtedly the counterpart of the similar shelf in the curves for the 2 per cent chromium and 2 per cent molybdenum steels (Figs. 16 and 17).

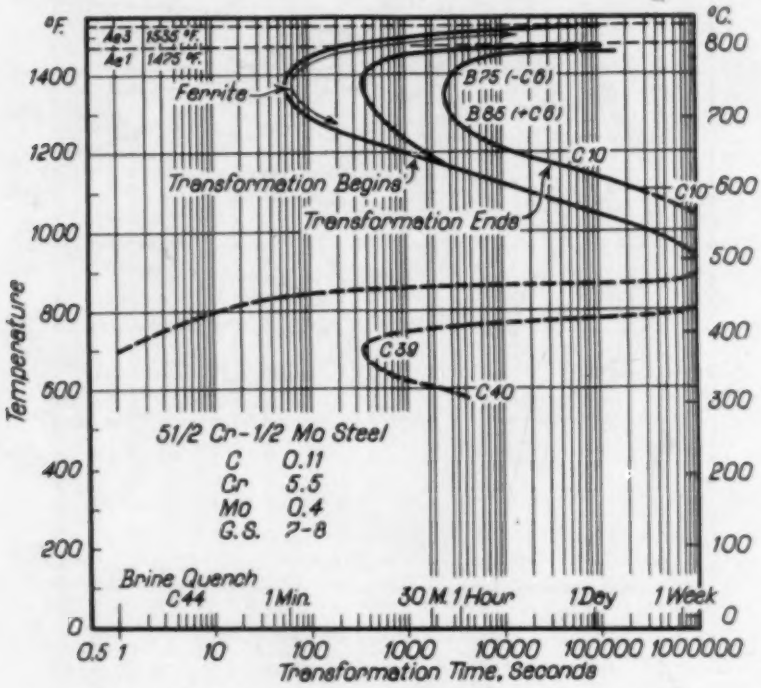


Fig. 28—Isothermal Transformation Curve for 5.5 Per Cent Chromium 0.5 Per Cent Molybdenum Steel.

The isothermal transformation curves of steels of this general class show that in such steels it is possible, by continuous cooling, to produce the acicular structure characteristic of the temperature range 500 to 950 degrees Fahr. (260 to 510 degrees Cent.); this can be accomplished on lower alloy and carbon steels only by rapidly quenching into a constant temperature bath and holding the steel there for the appropriate time, as is done in the process of austempering.

In a very recent paper Griffiths, Pfeil and Allen (68) present the results of an extensive investigation of this aspect of the heat treatment of alloy steels. Their work included determination of the transformation rates of nickel and chromium steels (0.30 per cent carbon) as well as determination of the mechanical properties of some of the "intermediate structures" which form in alloy steels at

levels between pearlite-forming and martensite-forming temperatures.

5.5 Per Cent Chromium-0.5 Per Cent Molybdenum Steel (0.11 Per Cent Carbon)—An attempt was made to determine the isothermal transformation curve of a typical 5.5 per cent chromium-0.5 per cent molybdenum steel and the results obtained are shown in Fig. 28. Owing to the low carbon content and the extremely sluggish behavior of this steel, the determination of its S-curve presents unusual experimental difficulties. However, we believe the upper

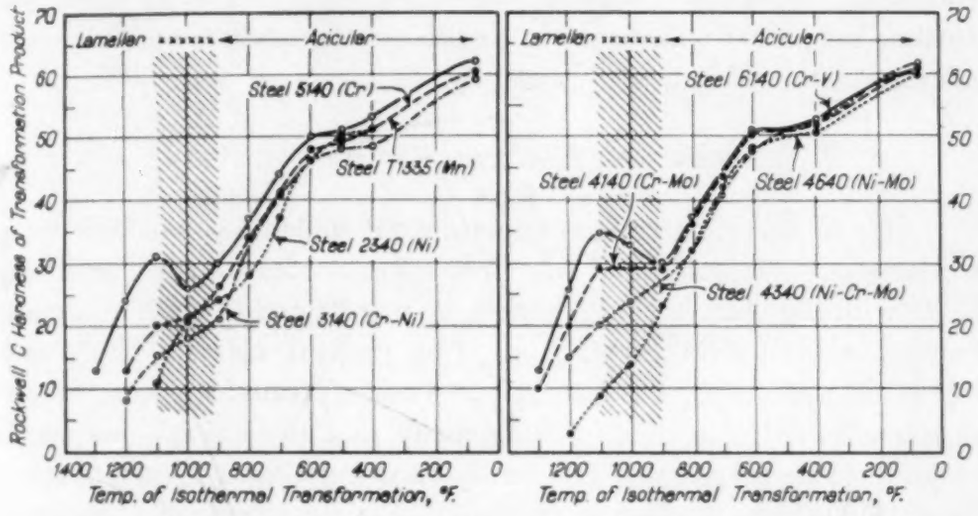


Fig. 29—Rockwell Hardness of Isothermal Transformation Products of the S.A.E. Steels Investigated.

portion of the curve (above 1000 degrees Fahr.) is substantially correct as shown; the lower portion is purely tentative and needs further investigation to establish the position of the lines with any degree of precision. In general, the curve is consistent with the views on the effect of carbon and alloy content expressed in the preceding sections of the lecture.

Hardness of Isothermal Transformation Products of S.A.E. Steels

The Rockwell C hardness of the products of isothermal transformation of the S.A.E. steels just discussed is shown graphically in Fig. 29; these curves are plotted on the same basis as those of Fig. 8. Note that they show an irregularity in the range 900 to 1100 degrees Fahr. (480 to 595 degrees Cent.), much the same as the corresponding curves for carbon steels (Fig. 8); the effect is particularly marked in steels containing strong carbide-forming elements

such as chromium, molybdenum and vanadium. Reference to the isothermal transformation curves of the S.A.E. steels shows that this irregularity in the sequence of hardness with transformation temperature tends to be associated most closely with the temperature range in which the structure changes from the lamellar to the acicular type; incidentally this occurs in the same general temperature range as the curious bay and promontory effects in the beginning and ending curves respectively. We believe that this is a manifestation of a fundamental behavior, common to both carbon and alloy steels, and further reference will be made to the question when the subject of microstructure is discussed presently.

Segregation, Banding, Homogenization

One of the most serious experimental difficulties encountered in working out the isothermal transformation curves of alloy steels has to do with the chemical segregation, as manifested by banding, which inevitably occurs in material of this general class. The metallographic method of estimating progress of transformation is particularly sensitive to such inhomogeneity in composition—one microscopic area in a specimen frequently showing almost complete transformation while an adjacent area may scarcely show even the beginning of transformation; the presumption is, of course, that the regions of austenite richer in dissolved carbon or alloy content transform more slowly than regions more dilute in these elements. Such a state of affairs makes estimation of the progress of transformation, for the steel as a whole, very difficult indeed, and it was suggested that the peculiar form of the curves might be due, in some part, to this microscopic inhomogeneity. Thus, the *beginning* curves conceivably might be representative of only the low alloy portions of the steel, while the *ending* curves might be representative of only the high alloy regions. Therefore, it was proposed that some of the S.A.E. steel curves be re-determined on material that had been homogenized by prolonged soaking at very high temperature. This was carried out on three typical steels, S.A.E. T-1335, S.A.E. 4140 and S.A.E. 4640, using an homogenizing treatment of 2200 to 2250 degrees Fahr. (1205 to 1235 degrees Cent.) for 48 hours in a substantially inert atmosphere. The microstructure of specimens suitably heat treated so as to reveal banding, if present, was used as the criterion of whether or not homogenization had been achieved; chem-

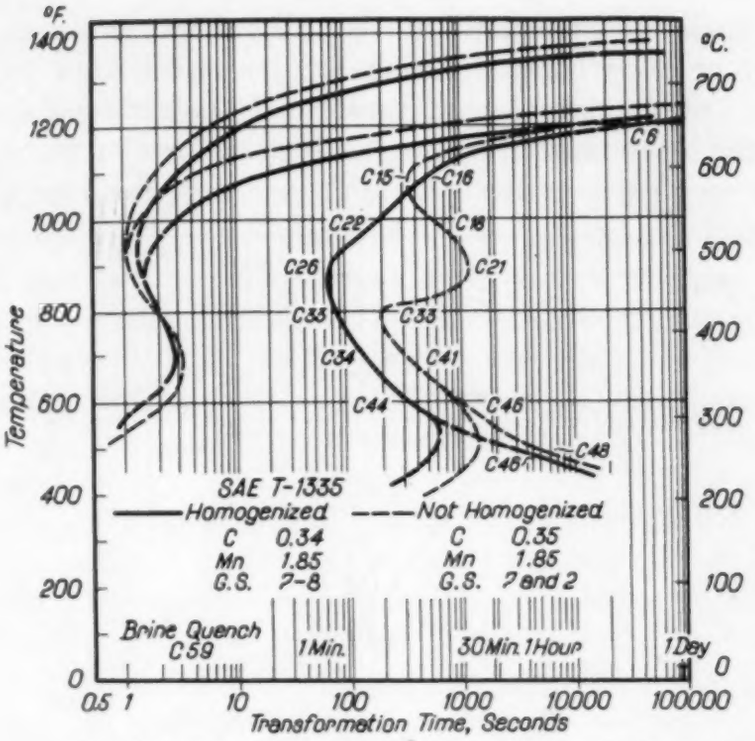


Fig. 30—Comparative Isothermal Transformation Curves for S.A.E. T-1335 Before and After Homogenization. Homogenized, Solid Lines; not Homogenized, Broken Lines.

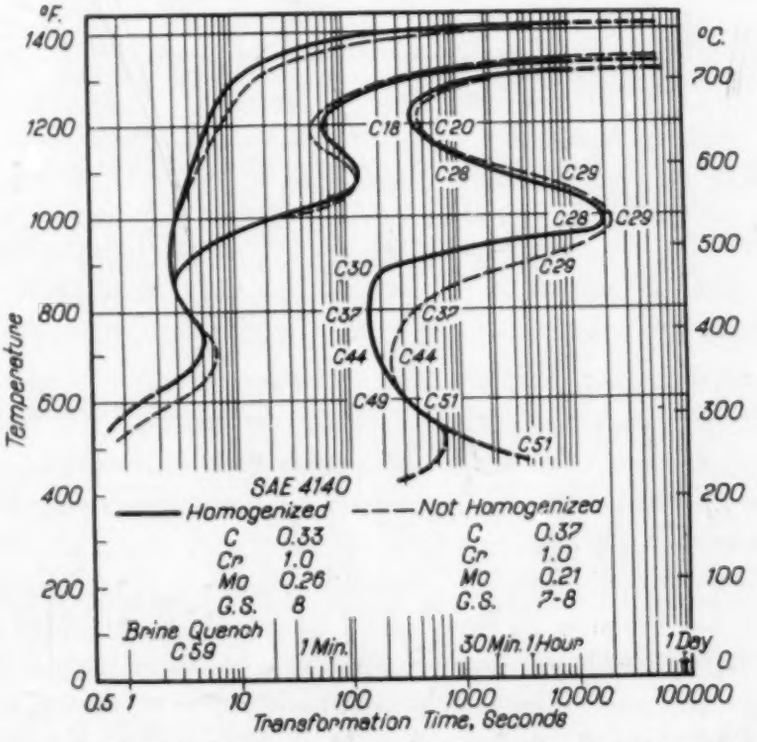


Fig. 31—Comparative Isothermal Transformation Curves for S.A.E. 4140 Before and After Homogenization. Homogenized, Solid Lines; not Homogenized, Broken Lines.

ical analysis indicated that the steels suffered no significant change of carbon or alloy content during the homogenization treatment. The same "austenitizing" temperature (1550 degrees Fahr.) was used for the determination of the "as homogenized" transformation curves as was used in the determination of the curves prior to

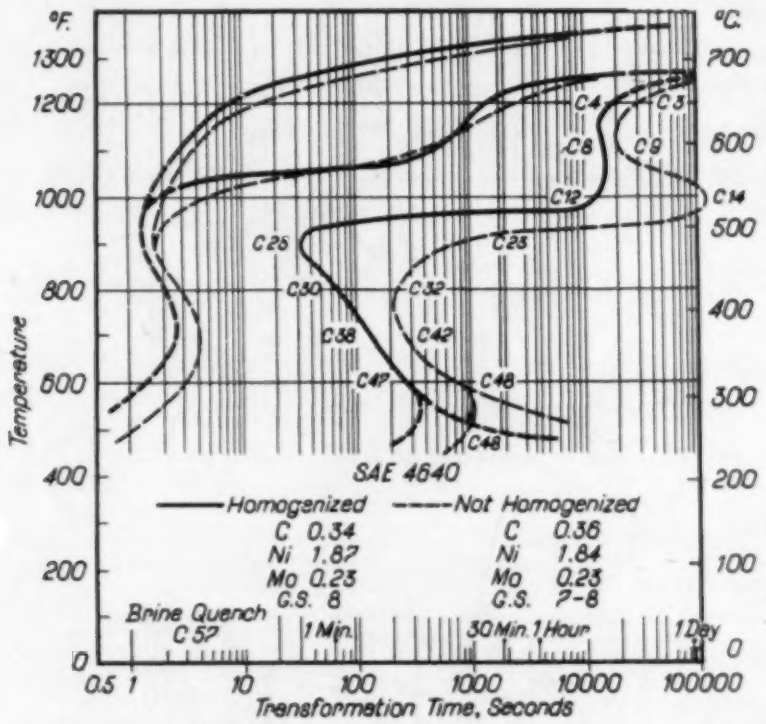


Fig. 32—Comparative Isothermal Transformation Curves for S.A.E. 4640 Before and After Homogenization. Homogenized, Solid Lines; not Homogenized Broken Lines.

homogenization; the austenite grain size obtained before and after homogenization is shown in Table II, the only significant change brought about by homogenization being the elimination of the mixed grain size in S.A.E. T-1335.

Table II
Austenite Grain Size at 1550 Degrees Fahr. (ASTM)

Steel	Before Homogenizing	After Homogenizing
S.A.E. T-1335 (Mn)	70% 7 and 30% 2	7-8
S.A.E. 4140 (Cr-Mo)	7-8	8
S.A.E. 4640 (Ni-Mo)	7-8	8

The isothermal transformation curves of these steels in both the homogenized and unhomogenized conditions are shown in Figs. 30, 31 and 32. In the case of S.A.E. T-1335 (Fig. 30) the time interval between beginning and end of transformation is appreciably

decreased and the promontory in the ending curve is substantially eliminated in the homogenized material, although it is difficult to say how much of this is due to the change in grain size or how much to homogenization; in any event, the results tend to suggest that the shape of the ending curve is strongly influenced by microscopic segregation. On the other hand, the curve for the S.A.E. 4140 steel (Fig. 31) is hardly influenced at all by homogenization, the only significant change being a slight acceleration of the end of transformation in the range 700 to 1000 degrees Fahr. (370 to 540 degrees Cent.); the marked promontory which is the outstanding feature of the ending curve for this steel certainly is not eliminated by homogenization. The S.A.E. 4640 steel (Fig. 32) behaved still differently; here both beginning and ending of transformation are somewhat accelerated by homogenization and the promontory in the ending curve is partially removed. The variability of these results indicates that further experimental study is needed before a clear picture of this aspect of the subject can be obtained. However, the experiments do indicate beyond doubt that the results of homogenizing treatments are dependent, to some extent, upon the tendency of the alloying elements present to form carbides and upon their rate of diffusion.

Microstructure of S.A.E. Steels

It is obviously impossible to present here an adequate discussion of the microstructures encountered in this investigation of the isothermal transformation of S.A.E. steels. In general, the same basic trends are found in these steels as in carbon steels; a series of lamellar structures is formed at the higher transformation temperatures, while acicular structures are formed at lower levels. In most of these steels, the intermediate temperature range yields structures which do not fit readily into the present scheme of metallographic nomenclature; moreover, there are differences in the structure of the different steels at the same temperature level and it is in the intermediate temperature range that these differences seem to be most pronounced; a sizable volume could be written about this aspect of the subject alone, without beginning to exhaust its possibilities.

As a compromise, we have elected to show the structures encountered at the different temperature levels in the S.A.E. 4140 steel as being fairly representative of most of the S.A.E. steels investigated. As a further limitation, we will show only the structure

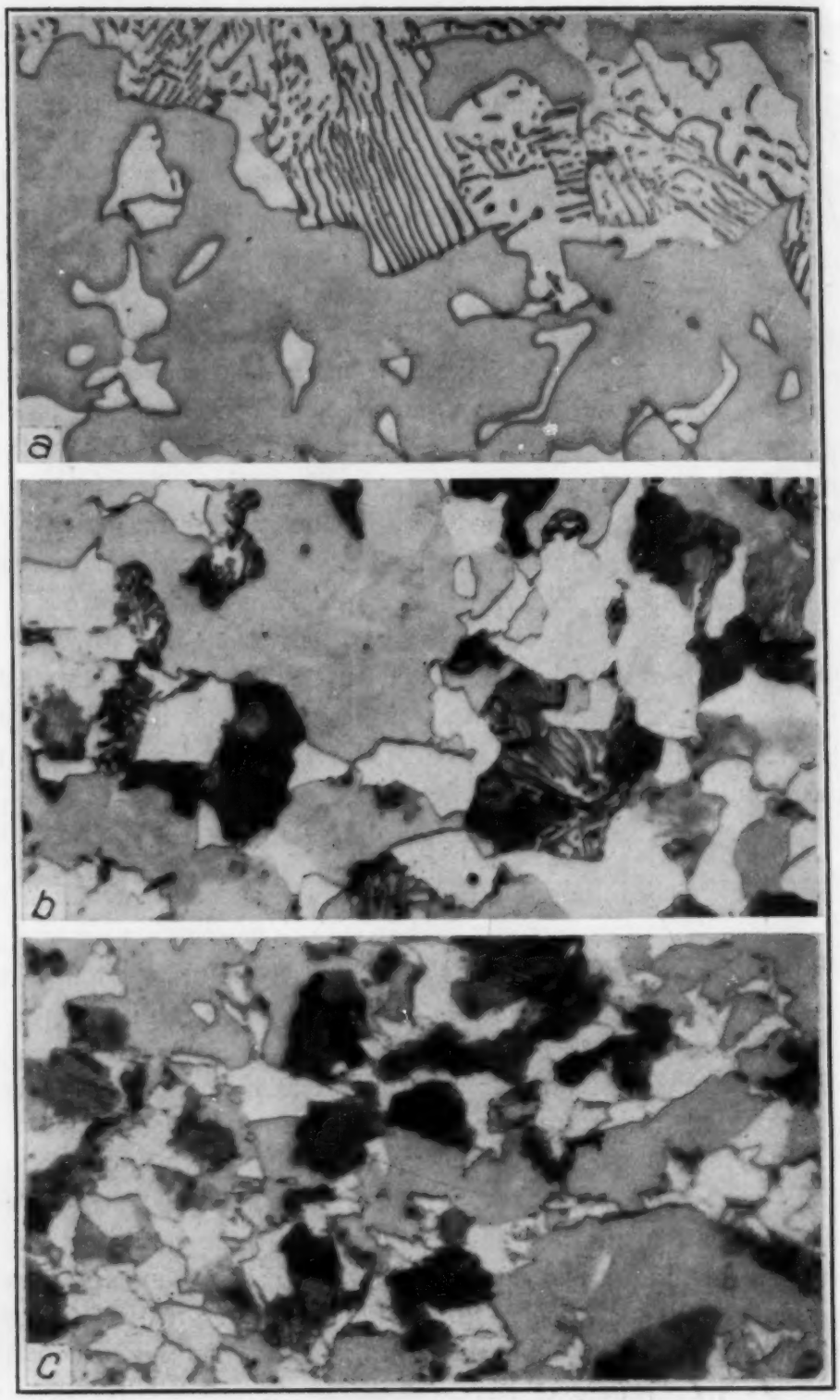


Fig. 33—Isothermal Transformation in S.A.E. 4140 Steel About 50 Per Cent Completed at, (a) 1350 Degrees Fahr. × 1000; (b) 1300 Degrees Fahr. × 1000; (c) 1200 Degrees Fahr. × 1000.

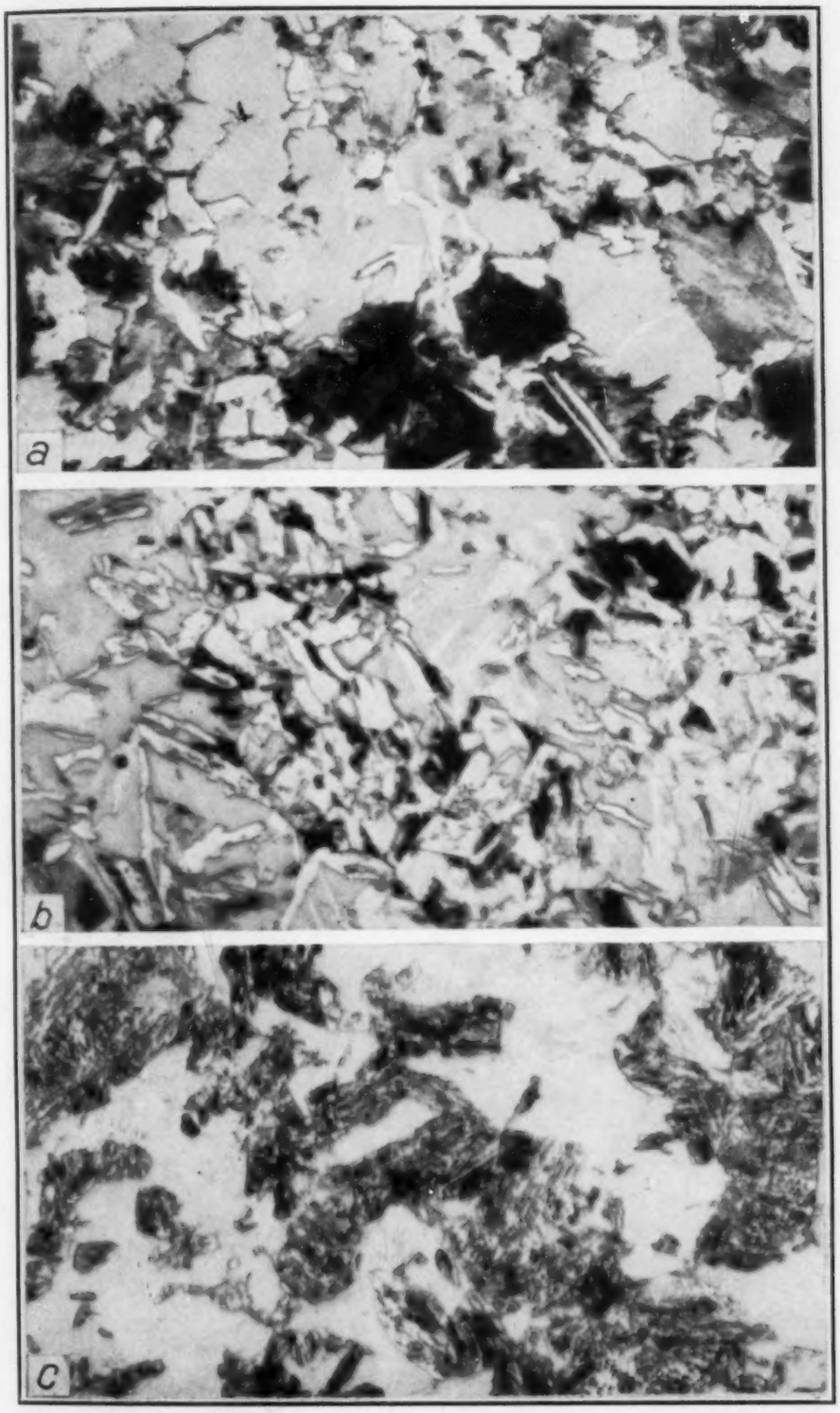


Fig. 34—Isothermal Transformation in S.A.E. 4140 Steel About 50 Per Cent Completed at, (a) 1100 Degrees Fahr. × 1000; (b) 1000 Degrees Fahr. × 1000; (c) 900 Degrees Fahr. × 1000.

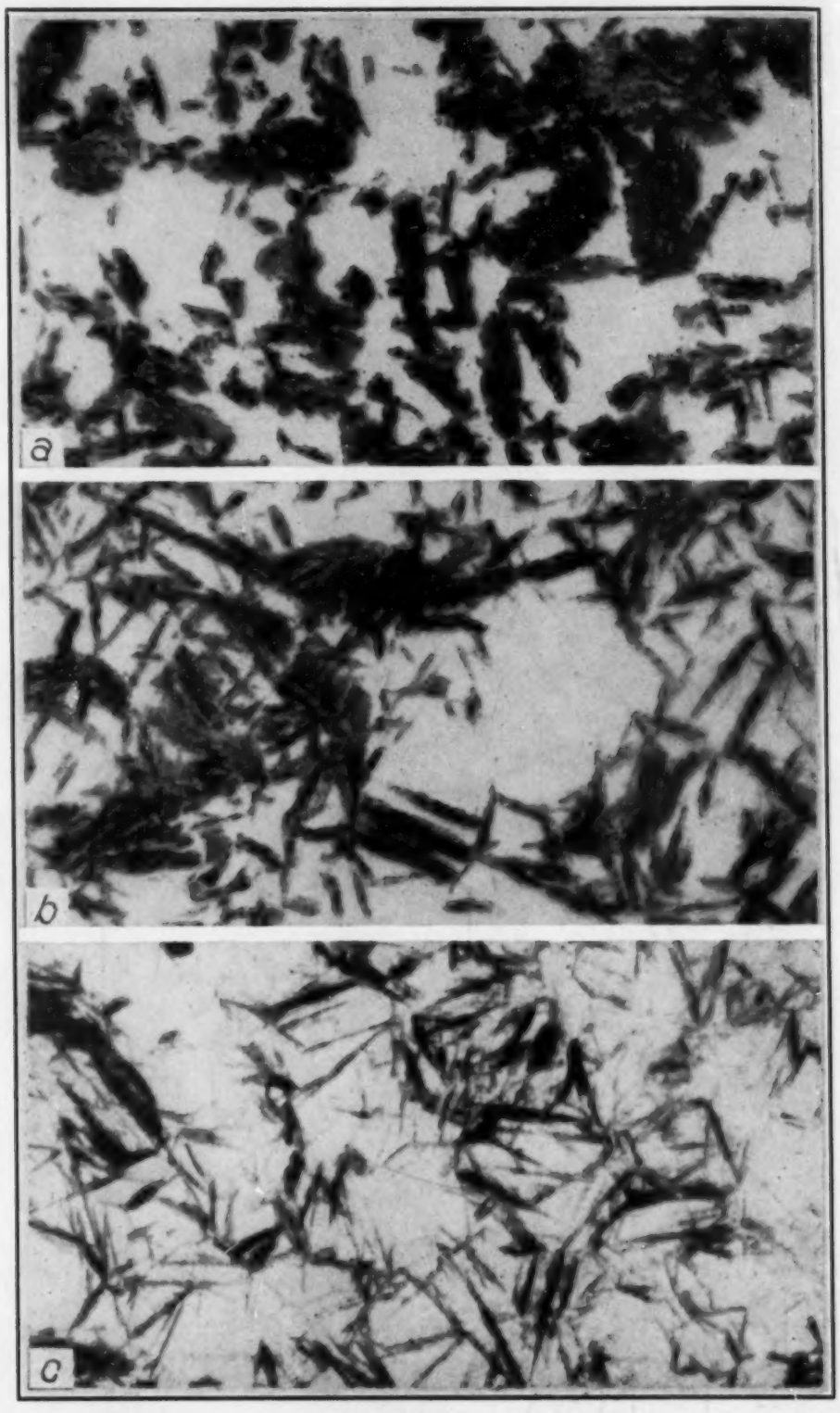


Fig. 35—Isothermal Transformation in S.A.E. 4140 Steel About 50 Per Cent Completed at, (a) 800 Degrees Fahr. × 1000; (b) 700 Degrees Fahr. × 1000; (c) 600 Degrees Fahr. × 1000.

obtained at each temperature level when the steel is about half transformed, since at this stage of the reaction both the mechanism of the transformation and the nature of the product can be most easily seen. These structures are shown in Figs. 33 to 35 inclusive, at a magnification of 1000 diameters.

At 1350 degrees Fahr. (730 degrees Cent.) the product of transformation consists of chunky proeutectoid ferrite and coarse, lamellar pearlite. As the transformation temperature is decreased to 1300 and 1200 degrees Fahr. (705 and 650 degrees Cent.), the ferrite continues to be chunky, although decreasing somewhat in volume and tending to outline the austenite grain size more clearly; at the same time, the pearlite becomes increasingly finer and more nodular as the transformation temperature is lowered. At 1100 degrees Fahr. (595 degrees Cent.) the ferrite decreases still further in volume and begins to show an acicular or Widmanstätten type of distribution, while the rapid-etching ferrite-carbide product (pearlite?) is now practically unresolvable and even begins, itself, to show a slight acicular tendency. At about 1000 degrees Fahr. (540 degrees Cent.) the rapid-etching product is quite acicular and, strangely enough, there is an unexpected increase in the volume of proeutectoid ferrite (if such it be), the distribution of which is distinctly acicular or Widmanstätten in character. In most of the alloy steels, particularly those rich in the carbide-forming elements, this acicular ferrite (?), which we have provisionally designated as "X", soon takes on a speckled appearance as though something were precipitating in it with increased holding time at temperature; this suggests that it may not be proeutectoid ferrite in the ordinary sense of the term, but rather some form of high temperature acicular product (bainite) which is reluctant to precipitate its carbon until an appreciable period of time at temperature has elapsed. It is worth noting that these particular structure effects occur at about the same temperature level as the bay in the beginning curve and the promontory in the ending curve which, in turn, seem to be associated with the irregularity in the sequence of hardness with transformation temperature (Fig. 29). We are convinced that all of these phenomena are intimately related and that continued study will ultimately reveal both their fundamental and practical significance.

At 900 degrees Fahr. (480 degrees Cent.) and at lower temperature levels the acicular ferrite ("X") observed in the vicinity of 1000 degrees Fahr. (540 degrees Cent.) disappears entirely and the

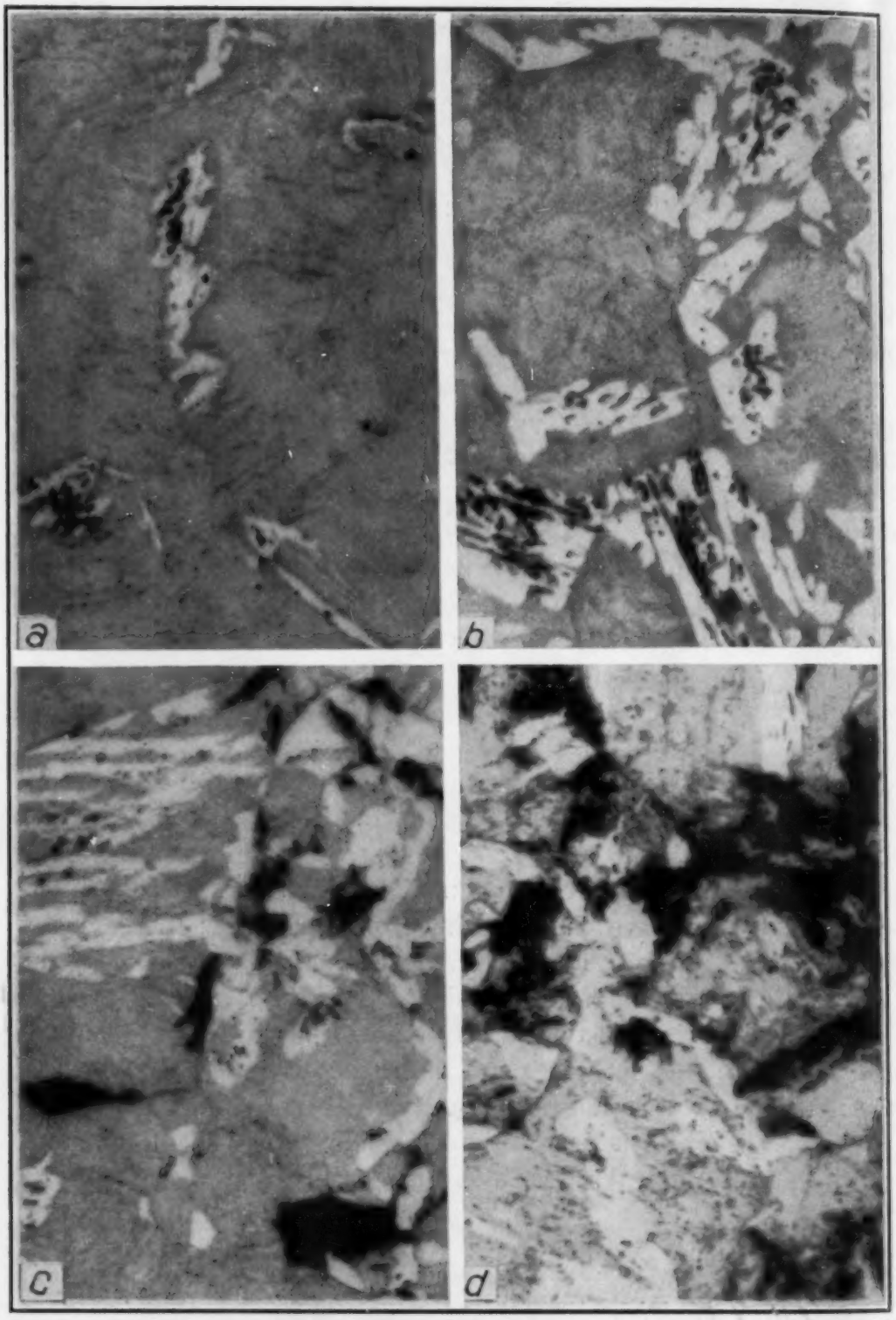


Fig. 36—Photomicrographs Illustrating Two Stages in the Isothermal Transformation of S.A.E. 4340 at 900 Degrees Fahr.

(a) Beginning of First Stage of Transformation. × 2000.
(b) First Stage Further Advanced. × 2000.
(c) Beginning of Second Stage of Transformation. × 2000.
(d) Second Stage Further Advanced. × 2000.

transformation product becomes more rapid-etching and more acicular in character much in accordance with the behavior of carbon steels. The transition zone between lamellar and acicular products is indicated on the isothermal transformation diagrams of the S.A.E. steels (Figs. 20 to 27) by a series of X's, and for the present we are inclined to leave this structure unnamed until further investigation reveals its true nature.

One more item in connection with this transition zone and the microstructure formed therein may be worth mentioning before leaving the subject. It has to do particularly with the mechanism of transformation at temperatures just below the "shelf" in the isothermal transformation curves of steels relatively high in carbide-forming elements, such as the 2 per cent chromium steel (Fig. 16) and S.A.E. 4340 (Fig. 27). Careful observations lead us to the tentative conclusion that the transformation proceeds in two fairly distinct stages in this temperature range, in a manner somewhat analogous to the two-stage behavior (first ferrite, followed by pearlite) characteristic of higher temperature levels. The first stage consists of the separation of acicular or Widmanstätten type ferrite ("X") which presently undergoes some sort of precipitation reaction, giving it the speckled appearance; then, when this stage is completed, the remainder of the transformation proceeds by the acicular process which yields a rapid-etching product similar in appearance to the familiar bainite of carbon steels. The photomicrographs of Fig. 36 illustrate these two stages in the transformation of S.A.E. 4340 steel at 900 degrees Fahr. (480 degrees Cent.); photomicrographs (a) and (b) show two examples in the first stage, in which only speckled ferrite ("X") appears, while photomicrographs (c) and (d) show two in the second stage, in which rapid-etching bainite is beginning to appear. This two-stage behavior is indicated on the isothermal transformation curves for the 2 per cent chromium and S.A.E. 4340 steels by a dotted line beneath the "shelf" at 950 degrees Fahr. (510 degrees Cent.), representing the beginning of the second stage of the reaction. We suspect that a similar state of affairs exists in many of the alloy steels but have been unable, so far, to determine it with sufficient precision to warrant indicating this behavior on the isothermal transformation diagrams.

Recapitulation and Some Questions for the Future

In this lecture we have attempted, first, to review briefly the

development and fundamental significance of isothermal transformation curves as applied to the heat treatment of steel, and second, to outline the major effects of alloying elements as revealed by such curves. In many instances these curves proved to be so individual that it is very difficult indeed to summarize the trends except in a quite general way. With the exception of cobalt, all of the alloying elements investigated retard the transformation of austenite in the Ar′ range, provided that prior to transformation the element is in real solid solution; and in general, the larger the amount of any given element in solution, the slower is the rate of transformation. The elements chromium, molybdenum and vanadium are most effective in this respect, with manganese next in order, while nickel and carbon exert a smaller, but appreciable, influence. Certain elements or combinations of elements, particularly those involving chromium or molybdenum, change the shape of the isothermal transformation curve in a most unexpected manner, giving rise to a curve which scarcely resembles the letter "S". From the standpoint of both theory and practice, these alloy steel curves have vastly different implications from the now-familiar S-curve for carbon steel, and therefore they should point the way to new and fruitful lines of investigation in the alloy steel field.

By placing the isothermal transformation diagrams of a number of typical alloy steels in the record at this time, it is hoped that greater interest in this approach to the subject will be aroused and that more widespread familiarity with these diagrams will result in clarification of some of the new questions posed by them.

Some of these questions center around *why* certain elements, or combinations of elements, alter the shape of the curves as they do, and what we may hope to be able to do in the future in the way of selecting alloy combinations to yield specific and predictable results. Other questions have more to do with the mode of transformation of *how* the mechanism by which a given structure forms out of austenite may influence its physical properties. Still other questions deal with the relationship between isothermal and continuous cooling transformation diagrams, a subject which has been merely mentioned in passing, but which is of paramount importance in applying isothermal transformation data to practical heat treating problems.

All of these questions, and many more, will occur to those who have been following this subject closely, and if such questions stimu-

late others to further experimentation along these lines, this lecture will have served a useful purpose.

Acknowledgments

Any investigation extending over a period of years involves the efforts of a large group of workers. It is my pleasant duty to acknowledge the many and varied contributions which my associates at the Research Laboratory of the United States Steel Corporation at Kearny, New Jersey, have made to this subject; it is obviously impracticable to name all of these men individually. However, I should particularly like to mention present and former associates, Messrs. R. A. Grange, J. M. Kiefer, R. V. Hilkert, R. H. Aborn, J. R. Vilella, E. G. Houston, R. F. Miller, R. F. Campbell, M. A. Hughes, H. J. Chapin, J. J. Rutherford, S. J. Kelley, all of whom took part in the preparation of the new material in this lecture. Messrs. A. J. Herzig, R. M. Parke and J. R. Blanchard of Climax Molybdenum Company, and Mr. L. S. Bergen of Crucible Steel Company of America have been most courteous and helpful in permitting us to compare our results on the S.A.E. steels with similar work of their own. I should like to call attention again to the earlier work and contributions of Dr. E. C. Bain, whose interest and faith in this approach to the subject has never failed; and lastly I wish to acknowledge gratefully the leadership and guidance of Dr. John Johnston, Director of Research, United States Steel Corporation, whose active support has been instrumental in bringing this subject to its present state of development.

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A DISCUSSION OF LEADED STEELS

By F. J. Robbins and G. R. Caskey

Abstract

This paper reports the results of physical and machine tests conducted on several analyses of lead-bearing steels in an effort to estimate the value of this type of steel for industrial applications. In evaluation of the physical character of this class of steel, the results of typical physical tests are compared to the average properties of nonleaded steels of similar base chemistry as found in standard references. Results of tests which show the comparative service strength of parts made from both leaded and nonleaded steels are reported.

The results of machine tests have been summarized in a machine chart in which the performance of each grade of lead-bearing steel is compared directly with the similar standard grade containing no lead. In an accompanying table are given suggested tool feeds to be used at the speeds shown in the machine chart. A detailed report is given of a machine test made on an automatic screw machine fabricating one part from several grades of leaded and nonleaded steels.

The paper discusses some of the shortcomings of lead-bearing steels as observed from time to time in the product of production heats, indicating that these are being overcome by improvements in manufacturing processes.

The conclusion is drawn that while a considerable amount of work remains to be done before the exact character and limitations of these steels will be fully known, lead-bearing steels have already demonstrated desirable characteristics such as to merit their use for many industrial applications.

Introduction

THIS paper is concerned with several selected grades of steel conforming to standard analysis of the Society of Automotive Engineers to which has been added lead. In all cases the specifica-

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tion worked to in the addition of lead is 0.15-0.30 per cent. All of the steels reported on here are materials which are the result of production practice. A great deal of work has been done in connection with the manufacture and application of lead-bearing steels although not a great deal of this has been reported on, due to the limited time it has been available. That information which has been reported on is noted in the references and will be referred to from time to time.

The paper is in no way concerned with the hazards of manufacture of lead-bearing steel. It is felt this question was answered in previous publications (1), (2), (4).[1] One of these papers discussed the problem of disposal of scrap which has been presented a number of times as of major importance. The introduction of any new product invariably presents problems of this type which are successfully solved by those responsible, if the product has such desirable characteristics as to warrant its acceptance by the user.

It is not the intention in this present effort to discuss the details of the manufacture of lead-bearing steels. It is felt that some effort now must be made to estimate the value of this type of steel to the user of the product in the light of the parts made from such steel. Further, it appears that with the great amount of data which has been collected some conclusion as to its comparative position among the other grades of steel long available can be drawn.

It is felt that this can best be done by a comparison of engineering data on lead-bearing steels with standard data of the same order which is available. To effect an unbiased comparison, data was gathered and is presented in such a way as to effect as easy and simple a comparison as possible with that published and considered standard references. The steels on which the many tests were run have in all cases been taken from stock to prevent the possible accusation of special practice in manufacture. This explains why the sizes used for test are not uniform and not always comparable.

It is recognized also that engineering data of the standard type does not always present an accurate and convincing picture of the ability of a steel to fulfill a given application. Some effort, therefore, has been made to supplement this information by applying standard tests to parts made from both types of materials and comparing the data developed.

To summarize briefly, the information presented in this paper

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

is divided into two parts. The first part is devoted to a comparison of engineering data which is intended to provide as accurate an estimate of leaded steels as is possible at present for those interested solely in the technical side of such a comparison. The second part is devoted to a consideration of the practical aspects of the fabrication of these steels.

Representative grades of each of the various types of leaded steel available have been selected for discussion. They cover Bessemer and open-hearth screw stocks, wherein the former machinability and economy of production are the all-important factors and in the latter where these factors must be compromised with carburizing quality and mechanical dependability. Included also are low and medium carbon types of the low sulphur steels where an improvement in machinability will represent a real advantage providing mechanical dependability will not be sacrificed. Following is a list of the steels referred to by their S.A.E. numbers. If lead has been added the S.A.E. number will be preceded by the word "leaded" and the standard analysis without lead will be referred to with the S.A.E. prefix.

S.A.E. X-1112
S.A.E. 1115
S.A.E. X-1335
S.A.E. X-1015
S.A.E. 1040

A consideration of mechanical property development should be preceded by a discussion of the heat treatment of leaded steels. Some mention has been made of the effect of lead additions on grain size (1), (2). There is a definitely refining action of lead on McQuaid-Ehn grain size. Usually this is a localized effect in steels made to a coarse grain practice and is further illustrated by the following photomicrographs which show the comparison of standard McQuaid-Ehn tests on the S.A.E. and leaded grades indicated. These photomicrographs were prepared to illustrate the characteristic modification of grain size resulting from the lead addition. Variables were present with respect to chemistry, sample preparation, etc., which preclude their use as a basis for other interpretations.

That the refining effect of lead on grain size is not uniform at all times is evidenced in these photomicrographs where the tendency toward a duplexed grain structure is observed. Steels made to a practice which would normally produce a coarse grain size may on

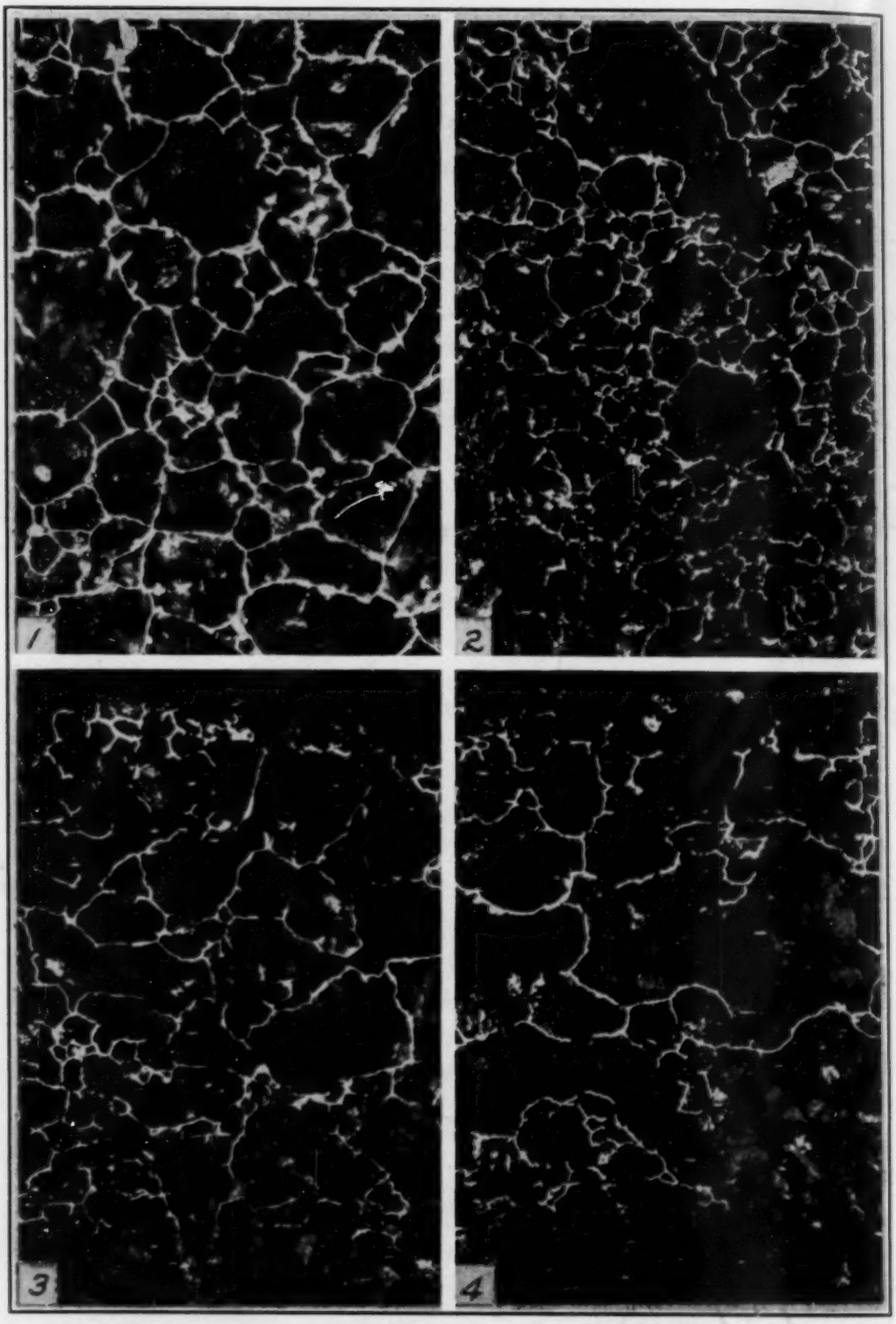


Fig. 1—Photomicrograph of S.A.E. X-1020 Standard McQuaid-Ehn Test. × 100.
Fig. 2—Photomicrograph of Leaded X-1020 Standard McQuaid-Ehn Test. × 100.
Fig. 3—Photomicrograph of S.A.E. 1115 Standard McQuaid-Ehn Test. × 100.
Fig. 4—Photomicrograph of Leaded 1115 Standard McQuaid-Ehn Test. × 100.

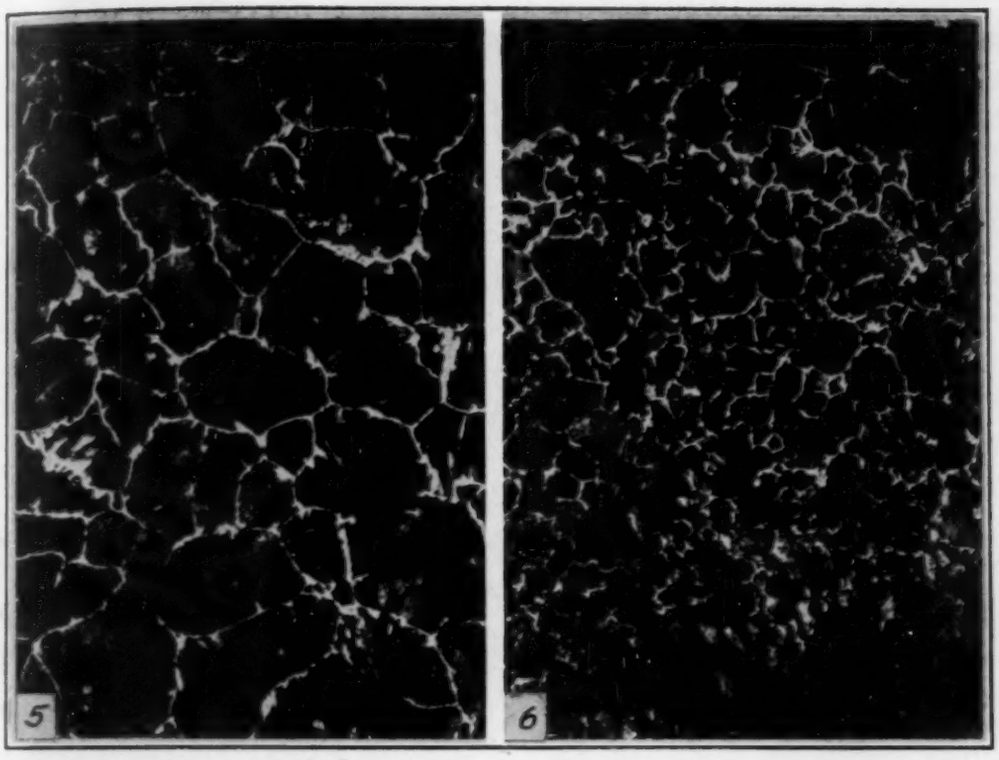


Fig. 5—Photomicrograph of S.A.E. 1040 Standard McQuaid-Ehn Test. × 100.
Fig. 6—Photomicrograph of Leaded 1040 Standard McQuaid-Ehn Test. × 100.

the addition of lead develop a duplexed grain structure, the proportion of fine grains ranging from a few per cent upward depending upon the exact deoxidation practice employed. Such a condition is not as noticeable in those steels made to a fine-grained practice. It is doubtful if this duplexing or refining of the grain has any evident effect upon the physical nature of the heat treated part, although theoretically some evidence of nonuniformity of hardness development might be expected. Generally speaking, open-hearth screw stocks and low carbon low sulphur steels are made to coarse-grained practice. These steels when fabricated are carburized and water-quenched which eliminates the effect of the duplexed structure which would show on a less drastically quenched part. Higher carbon steels are usually preferred to be fine grained and while refining effect is evident upon McQuaid-Ehn test it is found that the heat treated result does not show the expected effect. An occurrence of some considerable importance is noted in photomacrograph, Fig. 7.

This sample has been subjected to the noted heat treatment, and upon examination shows globules of lead which have oozed or been forced out of the piece. Probably the explanation is due to



Fig. 7—Globules of Lead on End of Piece. Pack Carburized at 1650 Degrees Fahr. for 7 Hours and Cooled in Box. × 3.

the higher coefficient of expansion of lead when compared to steel. This appears to be the result of lead segregation in considerably larger particle size than is found in leaded steels made to practice as noted in previous reports (1), (2). The size of voids left when the lead is squeezed out is a great deal larger than found in previous examinations. When made to ideal practice as found by experimentation lead particle size is very small, which is not the case in these samples from which lead is squeezed out. The parts illustrated were placed horizontally in the carburizing pot and very probably the lead particles were held in the position shown by the surrounding compound. Examination of a number of these samples shows a case beneath the lead globule and upon quenching during which the lead particles are lost a full hard martensitic case is developed.

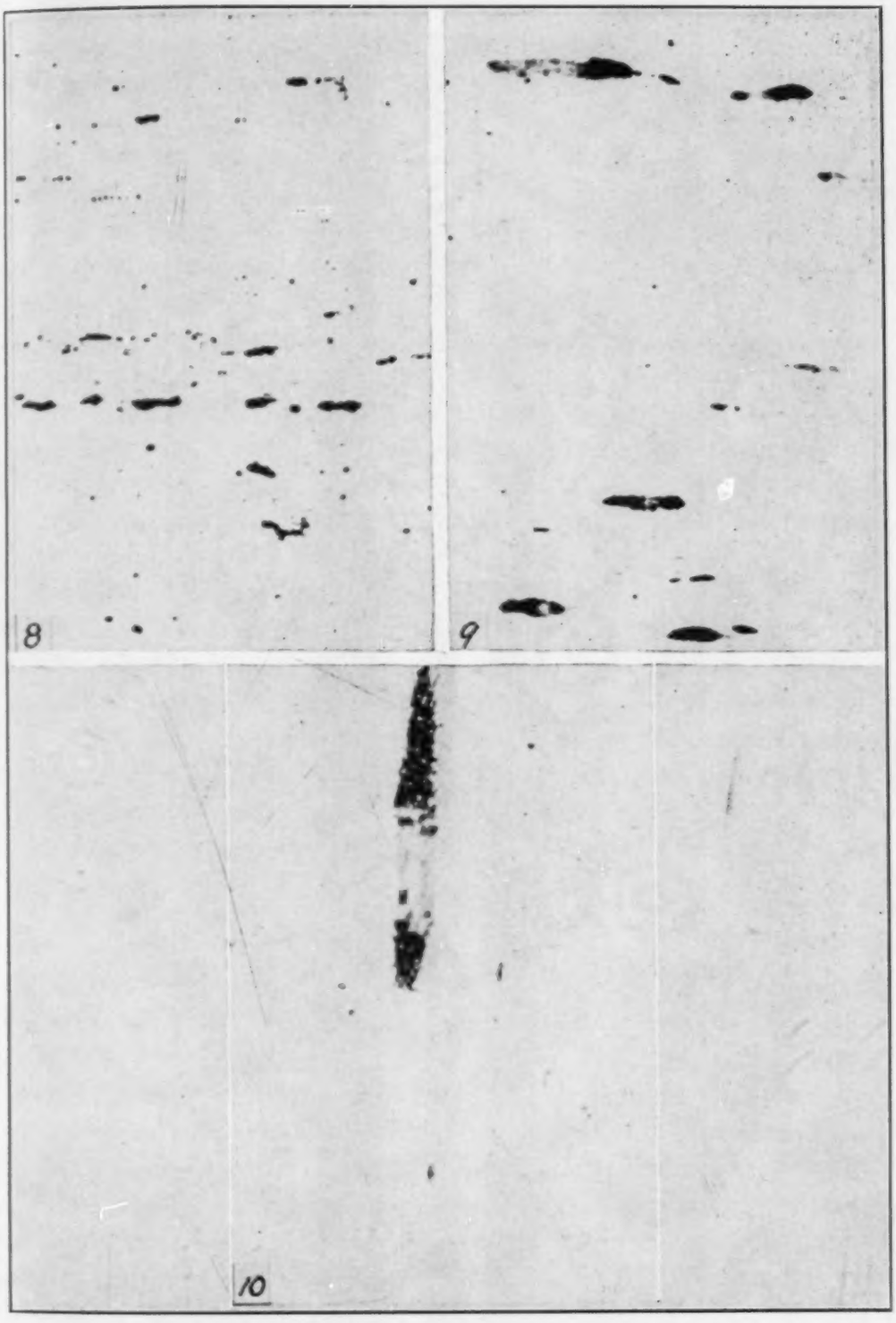


Fig. 8—Photomicrograph of Leaded X-1020 Steel. Unetched. × 100.
Fig. 9—Photomicrograph of Leaded 1115 Steel. Unetched. × 250.
Fig. 10—Photomicrograph of Leaded 1115 Steel. Same as Fig. 9. × 1000.

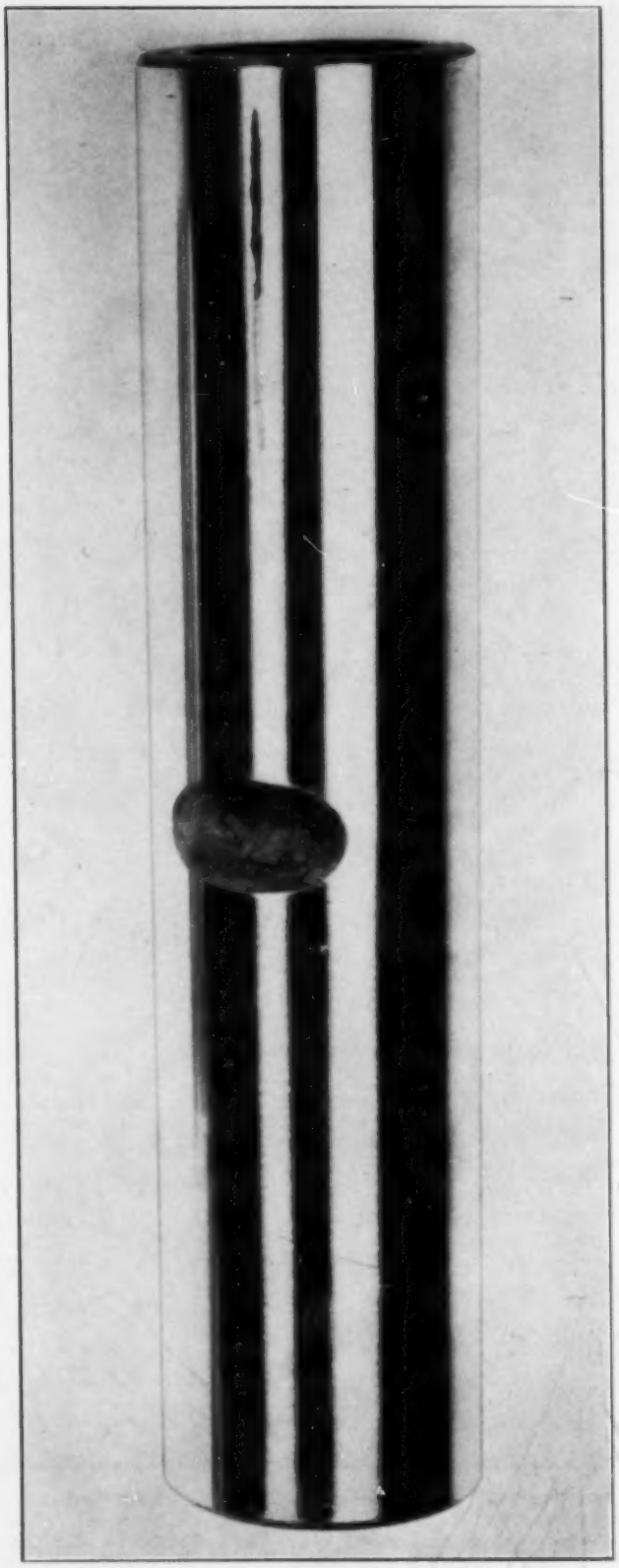


Fig. 11—Photomacrograph of Finished Piston Pin Showing Lead Segregation. Identification of Material Scraped from Inclusion was Made by Chemical Analysis.

Lead segregation appears to be one of the greatest difficulties encountered in the use of this type of steel and represents one of the problems which has been of major concern to the steel manufacturer.

In cases where lead segregation has been found to the detriment of the finished part a microscopic examination shows a condition as illustrated in Fig. 8. In the majority of the inclusions the presence of lead has been proved by methods which will be discussed in a paper now in preparation. At any rate this microscopic condition is present with segregation.

Figs. 9 and 10 are the results of a microscopic examination of material upon which no other evidence of lead segregation could be found.

In Fig. 11 is shown an unusually large lead segregation which was encountered by grinding the finished part. The lead had segregated a few thousandths under the surface. This is, of course, ample reason for rejection of the part and undoubtedly can be traced back to the method of lead addition made in the mold. Comments have been made in this regard (1), (2) and in steels where such segregation occurs the recommended practice has been deviated from as to method of addition, size of lead shot added, temperature, etc. Under circumstances where such practice has been adhered to, the tendency of lead to segregate is minimized and the lead is found to be present in particles of very small size which show no voids upon examination after subjection to heat treatment.

Engineering Test Data

Table I shows average mechanical properties found in a typical heat of leaded X-1112 Bessemer screw stock as compared to those average properties found in S.A.E. X-1112. It is not felt any especial significance can be assigned to a consideration of such characteristics of Bessemer steels principally because of the variations found to result from its method of manufacture. These data are presented merely for comparative purposes to indicate that under given conditions we need expect no essential difference in the two types of steel and that any application where the nonleaded Bessemer is now considered satisfactory will be found to possess equal character when made from the leaded product.

The addition of lead to this type of steel has not been found to produce any beneficial effects other than the improvement in ma-

Table I
Cold Drawn Bessemer ⅞-Inch Round

	S.A.E. X-1112	Leaded X-1112	Average to 1½ Inch Round Cold Drawn
Tensile strength, pounds per square inch..	89,910	87,920	85–102,000
Yield point, pounds per square inch	85,920	85,420	75– 90,000
Elongation in 2 inches	17.0	15.0	12– 20
Reduction of Area	41.9	40.4	40– 50
Brinell	207	192	170–212

Table II
S.A.E. 1115 treated in ⅞-Inch Round
All samples held 3½ hours at 1700 degrees Fahr. and given indicated treatment

	Tensile Strength Pounds Per Square Inch	Yield Point Pounds Per Square Inch	Elongation in 2 Inches	Reduction of Area	Charpy Impact	Brinell
Quench oil direct from pot	66,300	42,060	31.0	63.5	40/43	Surface 131 Center 131
Cooled in pot Reheat 1625° F. Quench water	82,920	54,600	23.0	61.1	35/36.5	Surface 146 Center 140
Cooled in pot Reheat 1625° F. Quench water Reheat 1425° F. Quench water	75,440	49,610	28.5	60.6	40/44	Surface 156 Center 143
Cooled in pot Reheat 1425° F. Quench water	83,520	55,960	21.0	52.7	31/34	Surface 174 Center 156

Table III
Leaded 1115 treated in ⅞-Inch Round
All samples held 3½ hours at 1700 degrees Fahr. and given indicated treatment

	Tensile Strength Pounds Per Square Inch	Yield Point Pounds Per Square Inch	Elongation in 2 Inches	Reduction of Area	Charpy Impact	Brinell
Quench oil direct from pot	64,240	46,810	36.0	65.9	38/40	Surface 126 Center 121
Cooled in pot Reheat 1625° F. Quench water	82,680	59,440	22.0	62.3	35.5/37	Surface 163 Center 156
Cooled in pot Reheat 1625° F. Quench water Reheat 1425° F. Quench water	73,340	48,760	31.0	65.9	41/41	Surface 149 Center 143
Cooled in pot Reheat 1425° F. Quench water	77,180	45,160	27.0	61.1	32/32	Surface 170 Center 143

Table IV

S.A.E. X-1015 treated in 1-inch Round

All samples held 8 hours at 1700 degrees Fahr. and given indicated treatment

	Tensile Strength Pounds Per Square Inch	Yield Point Pounds Per Square Inch	Elongation in 2 Inches	Reduction of Area	Izod
Quench oil direct from pot	109,000	59,000	15.5	39.5	16
Cooled in pot Reheat 1425° F. Quench water	88,000	45,000	29.0	64.4	..
Cooled in pot Reheat 1625° F. Quench water	97,000	49,500	24.5	45.8	13
Cooled in pot Reheat 1625° F. Quench water	106,000	53,900	22.0	49.0	33
Cooled in pot Reheat 1625° F. Quench water Reheat 1425° F. Quench water	86,000	46,600	31.0	67.2	51

Table V

Leaded X-1015 treated in 1-inch Round

All samples held 8 hours at 1700 degrees Fahr. and given indicated treatment

	Tensile Strength Pounds Per Square Inch	Yield Point Pounds Per Square Inch	Elongation in 2 Inches	Reduction of Area	Charpy Impact
Quench oil direct from pot	119,800	64,000	16.0	38.9	20/20
Cooled in pot Reheat 1425° F. Quench water	86,200	47,500	30.5	69.1	37/37
Cooled in pot Reheat 1425° F. Quench water	96,000	45,300	23.0	52.9	19/14
Cooled in pot Reheat 1625° F. Quench water	102,100	56,700	18.0 (broke near gage mark)	54.5	18/22
Cooled in pot Reheat 1625° F. Quench water Reheat 1425° F. Quench water	84,800	44,400	28.5	69.8	53/51

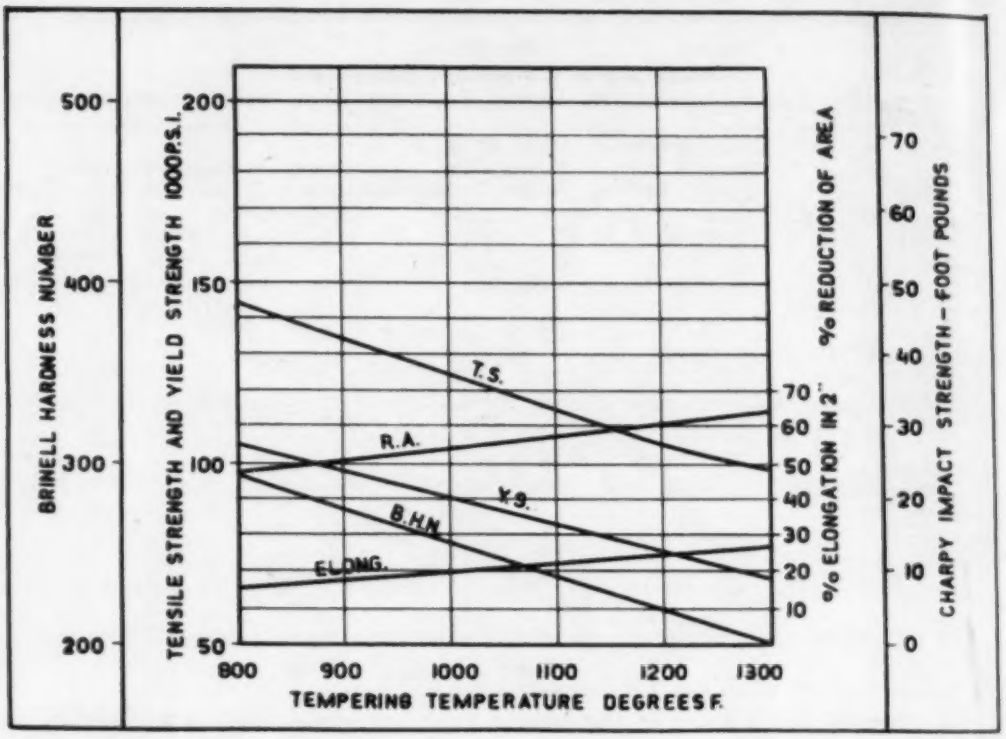
Table VI*

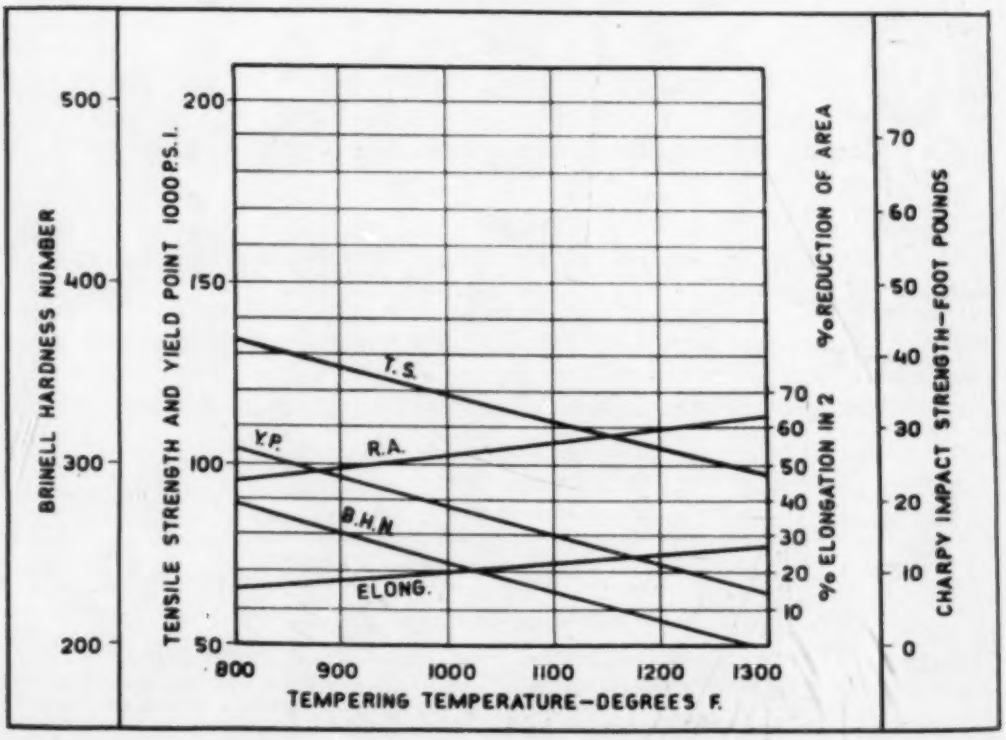
Crush test on piston pin

Length ..... 2⅞ inches
O.D. ..... 0.8135 inch
I.D. ..... 0.6265 inch
Average wall thickness ... 0.187 inch

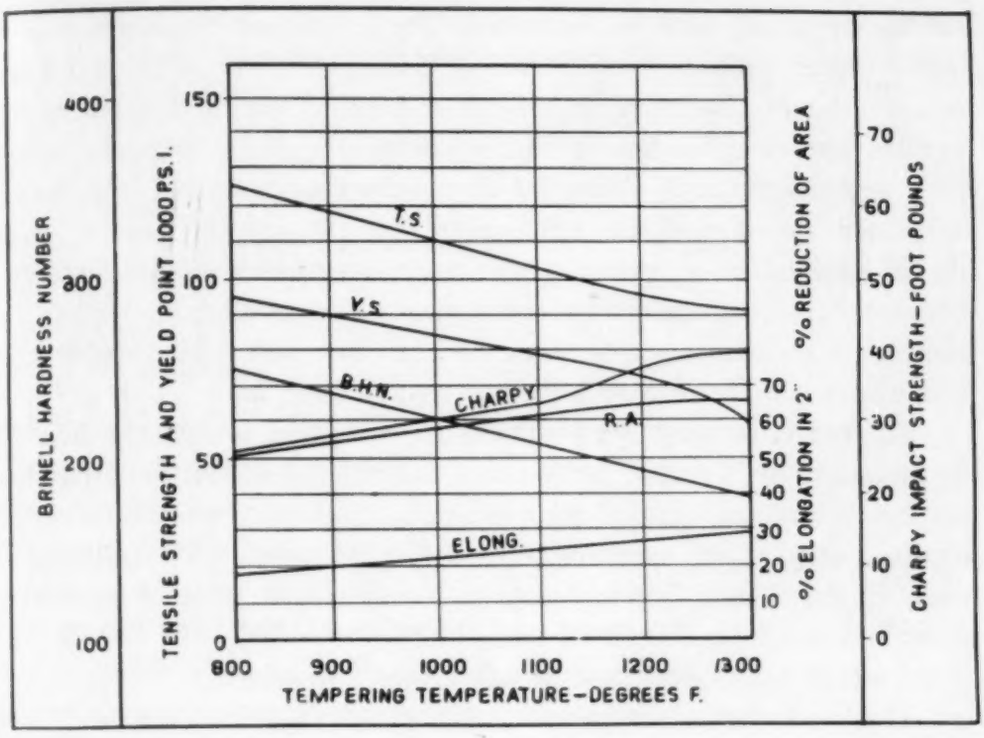
Test	S.A.E. X-1015	Leaded X-1015
1	39,070 pounds maximum load	46,410 pounds maximum load
2	39,110 pounds maximum load	44,630 pounds maximum load
3	39,520 pounds maximum load	44,380 pounds maximum load

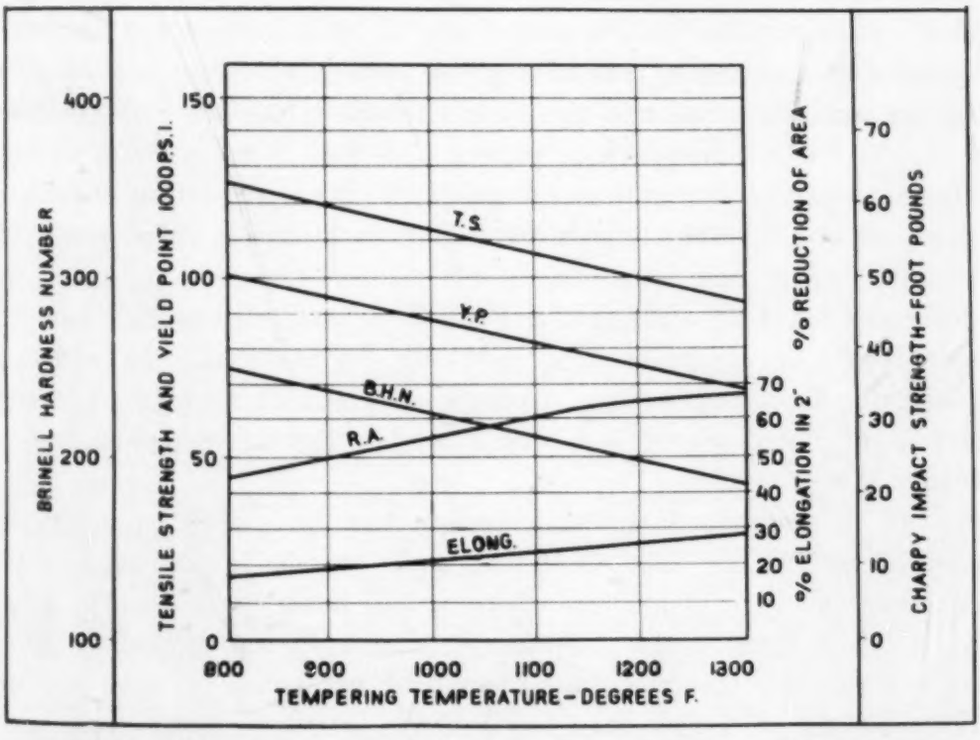
*Pins were selected from production runs in each case and came from runs at separate times. Samples were tested lying flat and failed suddenly into four pieces.





Figs. 12 and 13—Fig. 12 (upper) Shows Mechanical Property Development of Leaded 1040 Steel Compared to Fig. 13 (lower) Which is an Average Expectancy Chart for S.A.E. 1040 Gained from Information Already Published. (Ref. 5, 6, 7).





Figs. 14 and 15—Fig. 14 (upper) Shows the Characteristics of a Heat of Leaded X-1335 Compared to Fig. 15 (lower), Average Expectancy of S.A.E. X-1335. (Ref. 5, 6, 7).

chinability which will be discussed later. Leaded Bessemer will be found under average conditions to be subject to the same shortcomings as the nonleaded type. Such a product has not been recommended for case hardening and applications where strength, toughness and mechanical dependability were required and the leaded Bessemer could not be considered to possess properties making it applicable on parts where such requirements are essential. There are large numbers of parts now made from both leaded and nonleaded Bessemer screw stock of both low and high sulphur content where service history indicates its success.

In regard to open-hearth steels the situation is entirely different as their use is dictated by service conditions where hardenability, toughness and uniformity are essential. Such characteristics can be acquired only at the sacrifice of economy of production and ease of machining. The following data will show comparative properties under indicated conditions of leaded and nonleaded 1115 and X-1015 all of which were given a case hardening treatment.

It is felt that a comparison of a (controversial) relatively new product with data already published is more significant than the same kind of comparison made between special tests alone. For this reason mechanical property charts of leaded steels are compared directly to a chart of the same grade nonleaded composed of average expectancy properties as shown in various publications available, (5), (6), (7). In previous papers (1), (2) a comparison of bars from companion ingots was reported. Such a comparison eliminates many of the variables which are bound to be active in effecting the results shown, and is doubtless of value. Usually engineers and designers selecting a material for use in a particular application consult reputable references for properties considered. In order to facilitate direct comparison, a composite chart of average properties drawn as noted above has been placed alongside a typical test of leaded steel.

It is recognized that a criticism can be offered against this method in that the data on leaded steels are too limited and do not represent average properties which would show variables, the effect of which is many times considerable. A truly representative group of average expectancy curves cannot be presented because production of these steels has been too limited. Further, it was mentioned above that these tests were made on samples picked at random from production lots on mill schedule and therefore do represent average

Table VII*
Crush Test on Bushings Made from S.A.E. and Leaded 1115

Length	3.00 inches
O.D.	0.998 inch
I.D.	0.811 inch
Average wall thickness	0.187 inch

Test	S.A.E. 1115	Leaded 1115
1	24,850 pounds maximum load	25,570 pounds maximum load
2	24,510 pounds maximum load	25,710 pounds maximum load
3	23,900 pounds maximum load	25,380 pounds maximum load

*Heat treatment: Carburize 8 hours, cool in pot. (Drill out centers.) Reheat to 1600 degrees Fahr. Quench in oil. Reheat to 1400 degrees Fahr. Quench into water. Draw 300 degrees Fahr.

conditions as nearly as they can be had from the material available.

It does not appear necessary to offer detailed explanation of these comparisons since they are plainly evident in the curves shown. They show that additions of small amounts of lead to these steels has had no adverse effect upon the development of physical character by heat treatment. Many individual comments have been offered against leaded steels, particularly the medium carbon types, claiming very poor comparative properties. Investigation shows that even the nonleaded steels are subject to considerable variation in result as reported by many sources; this means that average results of nonleaded steels are generally lower than individual checks and while comparison of individual checks of leaded and nonleaded steels may be in favor of the latter, the leaded group does not show any great difference from average expectancy in the nonleaded.

Table VI and VII are illustrative of comparative strengths of parts made from leaded and nonleaded steels.

Machinability

A good deal has been said about the improvement in machinability as a result of adding a small percentage of lead. Previous publications (1), (2) have indicated in a general way the actual amount of improvement and just what this has meant in dollars-saving to the fabricator. It is felt that some effort can now be made to indicate this improvement quantitatively by means of a machine chart which will compare each grade of leaded and nonleaded steel. Fig. 16 shows the relative machinability of various grades of leaded and nonleaded steels based on comparative machine speeds (S.F.M.), S.A.E. 1112 being rated 100 per cent. It must be recognized that improvements incorporated in the past few years have resulted in

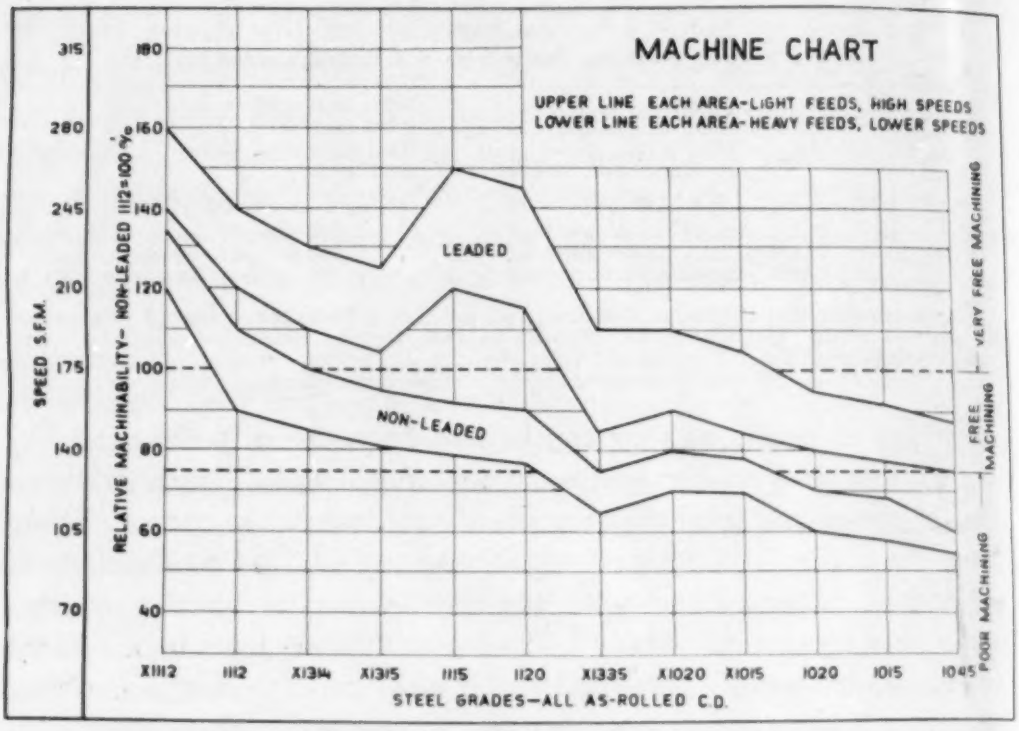
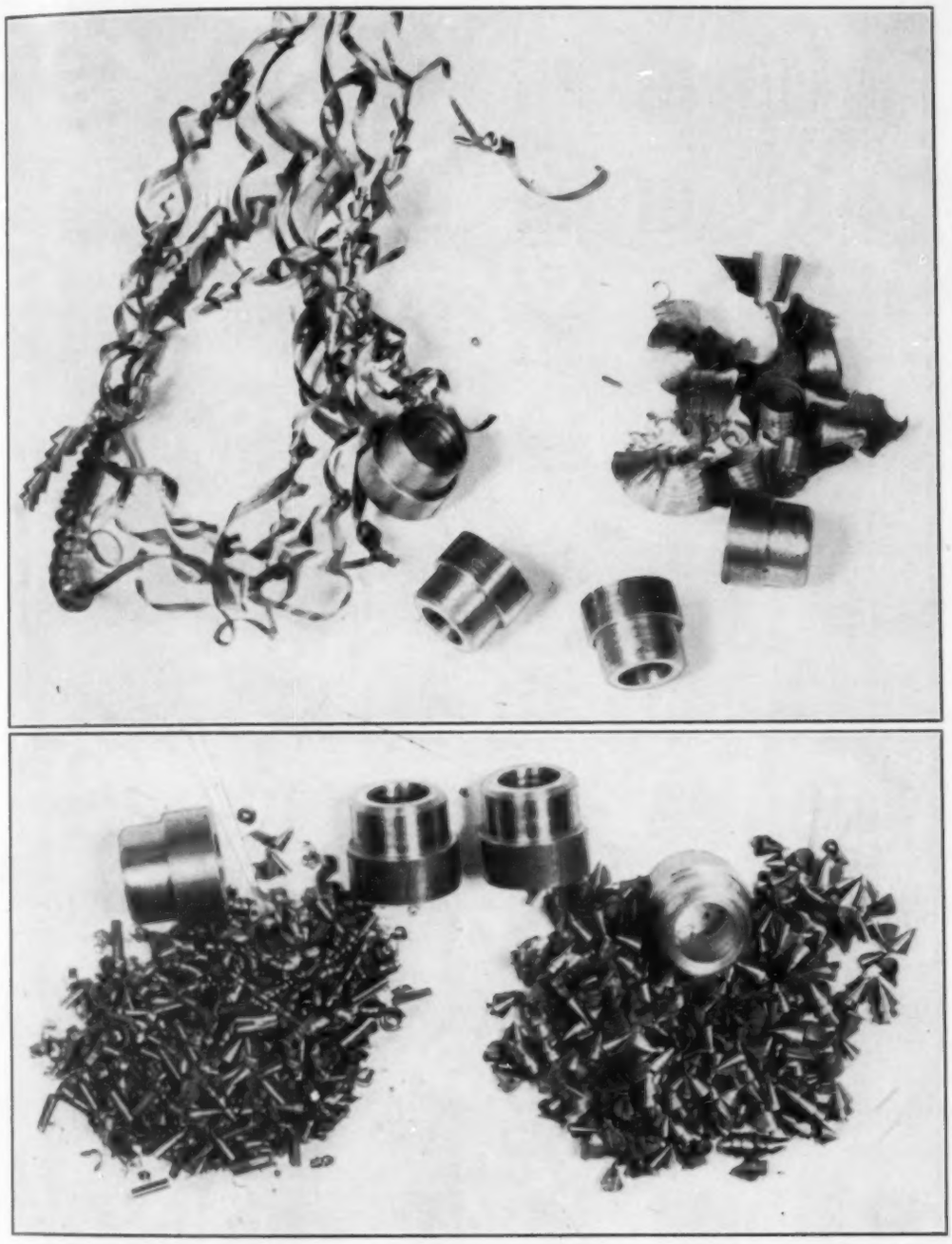


Fig. 16—Machine Chart for Leaded and Nonleaded Steels.

advancing the general machinability of all grades of steel. This improvement is taken into consideration by setting up S.A.E. 1112 at 175 S.F.M. speed and basing the other grades upon this representative speed which experience has shown to be average expectancy.

The chart is drawn to show the range over which speeds may be varied to include the many different operations which such steels are expected to withstand. It is common machine practice to vary machine speeds and tool feeds in order to produce certain specific requirements of a particular job. Table VIII and IX are presented for consideration with Fig. 16 to show what is considered a conservative estimate of tool feeds to be used with the speeds shown. Individual inclination seems to be a large factor in the choice of speeds and feeds although in some instances this choice is dictated by specific requirements as high accuracy, part finish, etc.

Further examination of Fig. 16 shows that among the standard S.A.E. steels only two grades, S.A.E. X-1112 and 1112, can be considered as exceptionally free machining while four grades can be considered as free machining. The balance of those shown are in general nonfree machining. It is to be noted that the addition of lead to these grades has simply shifted the entire group upward so



Figs. 17 and 18—Photographs Illustrating the Difference in Form of Chips Resulting from Forming and Drilling Operations in Fabricating the Parts Illustrated. In Each Case the Chips from Drilling Are Placed on the Left Side of the Picture. Upper —S.A.E. 1120. Lower—Leaded 1120.

that even the poorest of the group, S.A.E. 1045 unannealed, now falls into the free machining group and that in the exceptionally free machining group are now found five grades.

This chart is based upon production results over a wide variety of jobs and embracing all types of tooling operations. A number

Table VIII

	X-1112		Leaded X-1112		1112		Leaded 1112		X-1314		Leaded X-1314	
	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds
Box Tool Blades Depths												
0 to 1/8	0.0080	0.0040	0.0100	0.0040	0.0070	0.0030	0.0080	0.0040	0.0055	0.0030	0.0060	0.0030
1/8 to 3/8	0.0070	0.0030	0.0080	0.0030	0.0060	0.0025	0.0070	0.0030	0.0045	0.0020	0.0050	0.0025
3/8 to 1/2	0.0060	0.0025	0.0070	0.0025	0.0050	0.0020	0.0060	0.0025	0.0035	0.00175	0.0040	0.00175
Cut Off Widths												
1/16	0.0030	0.0016	0.0035	0.00125	0.0025	0.0008	0.0030	0.0010	0.00175	0.0007	0.0020	0.0008
1/8	0.0035	0.00125	0.0040	0.0015	0.0030	0.0010	0.0035	0.00125	0.0020	0.0010	0.0022	0.0010
1/8	0.0035	0.0015	0.0040	0.00175	0.0030	0.00125	0.0035	0.0015	0.0020	0.0012	0.0022	0.0012
H.S. Twist Drills												
0 to 1/8	0.0030	0.0010	0.0035	0.00125	0.0025	0.0008	0.0030	0.0010	0.0020	0.0005	0.0025	0.0007
1/8 to 1/4	0.0070	0.0030	0.0080	0.0035	0.0060	0.0025	0.0070	0.0030	0.0045	0.0015	0.0050	0.0017
1/4 to 3/4	0.0080	0.0035	0.0090	0.0040	0.0070	0.0030	0.0080	0.0035	0.0050	0.0023	0.0055	0.0023
3/4 to 1 1/4	0.0100	0.0040	0.0120	0.0050	0.0090	0.0035	0.0100	0.0040	0.0070	0.0020	0.0075	0.0025
Rough Forms Widths												
0 to 1/8	0.0035	0.0015	0.0040	0.00175	0.0030	0.0010	0.0035	0.0015	0.0023	0.0008	0.0025	0.0009
1/8 to 5/8	0.0030	0.00125	0.0035	0.0015	0.0025	0.0008	0.0030	0.00125	0.0020	0.0006	0.0022	0.0007
5/8 to 7/8	0.0020	0.0010	0.0025	0.00125	0.00175	0.0006	0.0020	0.0010	0.0015	0.0004	0.0016	0.0005
7/8 to 1 1/4	0.0017	0.0008	0.0020	0.0010	0.0015	0.0004	0.0017	0.0006	0.0010	0.0002	0.0012	0.0003
Finish Forms Widths												
0 to 1/8	0.0030	0.0010	0.0035	0.00125	0.0025	0.0008	0.0030	0.0010	0.0020	0.0006	0.0022	0.0007
1/8 to 5/8	0.0025	0.0008	0.0030	0.0010	0.00175	0.0006	0.0025	0.0008	0.0015	0.0005	0.0017	0.0006
5/8 to 7/8	0.00175	0.0006	0.0020	0.0008	0.0015	0.0004	0.00175	0.0006	0.0010	0.0004	0.0012	0.0005
7/8 to 1 1/4	0.0015	0.0004	0.00175	0.0005	0.0010	0.0003	0.0015	0.0004	0.0008	0.0002	0.0009	0.0003

Table VIII—Continued

	X-1315		Leaded X-1315		1115		Leaded 1115		1120		Leaded 1120	
	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds
Box Tool Blades Depths												
0 to 1/8	0.0050	0.0030	0.0060	0.0030	0.0050	0.0030	0.0070	0.0030	0.0050	0.0030	0.0070	0.0030
1/8 to 3/16	0.0045	0.0020	0.0050	0.0020	0.0045	0.0020	0.0060	0.0025	0.0045	0.0020	0.0060	0.0025
3/16 to 1/2	0.0035	0.00175	0.0040	0.00175	0.0035	0.00175	0.0050	0.0020	0.0035	0.00175	0.0050	0.0020
Cut Off Widths												
1/32	0.00175	0.0007	0.0020	0.0008	0.00175	0.0007	0.0025	0.0008	0.00175	0.0007	0.0025	0.0008
1/8	0.0020	0.0010	0.0022	0.0010	0.0020	0.0010	0.0030	0.0010	0.0020	0.0010	0.0030	0.0010
1/16	0.0020	0.0012	0.0023	0.0012	0.0020	0.0012	0.0030	0.00125	0.0020	0.0012	0.0030	0.00125
H.S. Twist Drills												
0 to 1/8	0.0020	0.0005	0.0025	0.0007	0.0020	0.0005	0.0025	0.0008	0.0020	0.0005	0.0025	0.0008
1/8 to 3/8	0.0045	0.0015	0.0050	0.0017	0.0045	0.0015	0.0060	0.0025	0.0045	0.0015	0.0060	0.0025
3/8 to 3/4	0.0050	0.0023	0.0055	0.0023	0.0050	0.0023	0.0070	0.0030	0.0050	0.0023	0.0070	0.0030
3/4 to 1 1/4	0.0070	0.0020	0.0075	0.0025	0.0070	0.0020	0.0090	0.0035	0.0070	0.0020	0.0090	0.0035
Rough Forms Widths												
0 to 1/8	0.0023	0.0008	0.0025	0.0009	0.0023	0.0008	0.0030	0.0010	0.0023	0.0008	0.0030	0.0010
1/8 to 5/8	0.0020	0.0006	0.0022	0.0007	0.0020	0.0006	0.0025	0.0008	0.0020	0.0006	0.0025	0.0008
5/8 to 7/8	0.0015	0.0004	0.0016	0.0005	0.0015	0.0004	0.00175	0.0006	0.0015	0.0004	0.00175	0.0006
7/8 to 1 1/4	0.0010	0.0002	0.0012	0.0003	0.0010	0.0002	0.0015	0.0004	0.0010	0.0002	0.0015	0.0004
Finish Forms Widths												
0 to 1/8	0.0020	0.0006	0.0022	0.0007	0.0020	0.0006	0.0025	0.0008	0.0020	0.0006	0.0025	0.0008
1/8 to 5/8	0.0015	0.0005	0.0017	0.0006	0.0015	0.0005	0.00175	0.0006	0.0015	0.0005	0.00175	0.0006
5/8 to 7/8	0.0012	0.0004	0.0012	0.0005	0.0012	0.0004	0.0015	0.0005	0.0012	0.0004	0.0015	0.0005
7/8 to 1 1/4	0.0008	0.0002	0.0009	0.0003	0.0008	0.0002	0.0010	0.0003	0.0008	0.0002	0.0010	0.0003

Table IX

	X-1335		Leaded X-1335		X-1020		Leaded X-1020		X-1015		Leaded X-1015	
	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds	Low Speed Feeds	High Speed Feeds
Box Tool Blades Depths												
0 to 1/8	0.0045	0.0027	0.0050	0.0030	0.0047	0.0030	0.0055	0.0035	0.0046	0.0028	0.0053	0.0034
1/8 to 3/8	0.0040	0.0020	0.0045	0.0025	0.0044	0.0025	0.0050	0.0030	0.0043	0.0023	0.0048	0.0028
3/8 to 1/2	0.0035	0.0015	0.0040	0.0020	0.0040	0.0017	0.0045	0.0025	0.0038	0.0015	0.0044	0.0025
Cut Off Widths												
1/16	0.0015	0.0007	0.0017	0.0009	0.0017	0.0007	0.0019	0.0008	0.0016	0.0010	0.0018	0.0011
1/8	0.0017	0.0010	0.0020	0.0012	0.0020	0.0010	0.0022	0.0012	0.0020	0.0012	0.0021	0.0013
3/16	0.0020	0.0012	0.0023	0.0014	0.0022	0.0012	0.0023	0.0014	0.0022	0.0015	0.0022	0.0016
H.S. Twist Drills												
0 to 1/8	0.0016	0.0004	0.0018	0.0005	0.0017	0.0005	0.0019	0.0006	0.0016	0.0004	0.0018	0.0005
1/8 to 3/8	0.0040	0.0012	0.0042	0.0014	0.0041	0.0013	0.0043	0.0015	0.0041	0.0013	0.0042	0.0014
3/8 to 3/4	0.0045	0.0020	0.0047	0.0022	0.0046	0.0022	0.0048	0.0023	0.0045	0.0021	0.0047	0.0022
3/4 to 1 1/4	0.0065	0.0025	0.0067	0.0027	0.0066	0.0026	0.0068	0.0028	0.0065	0.0025	0.0067	0.0027
Rough Forms Widths												
0 to 3/16	0.0021	0.0007	0.0023	0.0008	0.0022	0.0008	0.0024	0.0009	0.0021	0.0007	0.0023	0.0008
3/16 to 5/8	0.0018	0.0005	0.0019	0.0006	0.0019	0.0006	0.0020	0.0007	0.0018	0.0005	0.0019	0.0006
5/8 to 7/8	0.0013	0.0003	0.0014	0.0004	0.0014	0.0004	0.0015	0.0005	0.0013	0.0003	0.0014	0.0004
7/8 to 1 1/4	0.0009	0.0002	0.0010	0.0002	0.0010	0.0002	0.0011	0.0003	0.0009	0.0002	0.0010	0.0002
Finish Forms Widths												
0 to 3/16	0.0018	0.0005	0.0020	0.0006	0.0020	0.0008	0.0021	0.0009	0.0019	0.0008	0.0021	0.0009
3/16 to 5/8	0.0014	0.0004	0.0016	0.0005	0.0016	0.0007	0.0017	0.0007	0.0015	0.0006	0.0017	0.0007
5/8 to 7/8	0.0010	0.0003	0.0012	0.0004	0.0012	0.0005	0.0013	0.0005	0.0011	0.0005	0.0013	0.0005
7/8 to 1 1/4	0.0007	0.0002	0.0008	0.0003	0.0009	0.0003	0.0010	0.0003	0.0008	0.0003	0.0010	0.0003

Table IX—Continued

	1020 Low Speed Feeds	1020 High Speed Feeds	Leaded 1020 Low Speed Feeds	Leaded 1020 High Speed Feeds	1015 Low Speed Feeds	1015 High Speed Feeds	Leaded 1015 Low Speed Feeds	Leaded 1015 High Speed Feeds	1045 Unannealed Low Speed Feeds	1045 Unannealed High Speed Feeds	Leaded 1045 Low Speed Feeds	Leaded 1045 High Speed Feeds
Box Tool Blades Depths												
0 to 1/8	0.0045	0.0027	0.0055	0.0034	0.0043	0.0025	0.0052	0.0032	0.0041	0.0023	0.0050	0.0032
1/8 to 3/8	0.0040	0.0020	0.0050	0.0028	0.0038	0.0017	0.0048	0.0026	0.0036	0.0015	0.0045	0.0026
3/8 to 1/2	0.0035	0.0015	0.0045	0.0023	0.0032	0.0013	0.0043	0.0021	0.0030	0.0010	0.0040	0.0021
Cut Off Widths												
1/16	0.0015	0.0009	0.0017	0.0010	0.0014	0.0008	0.0016	0.0009	0.0012	0.0006	0.0014	0.0007
1/8	0.0019	0.0011	0.0020	0.0012	0.0018	0.0010	0.0019	0.0011	0.0016	0.0008	0.0017	0.0009
3/16	0.0021	0.0014	0.0021	0.0015	0.0020	0.0013	0.0020	0.0014	0.0018	0.0010	0.0018	0.0014
H.S. Twist Drills												
0 to 1/8	0.0015	0.0003	0.0017	0.0004	0.0014	0.0002	0.0016	0.0003	0.0013	0.0002	0.0015	0.0003
1/8 to 3/8	0.0040	0.0012	0.0041	0.0013	0.0039	0.0011	0.0040	0.0012	0.0038	0.0010	0.0039	0.0012
3/8 to 3/4	0.0044	0.0020	0.0046	0.0021	0.0043	0.0019	0.0045	0.0020	0.0042	0.0018	0.0044	0.0020
3/4 to 1 1/4	0.0064	0.0024	0.0066	0.0026	0.0063	0.0023	0.0065	0.0025	0.0062	0.0023	0.0064	0.0024
Rough Forms Widths												
0 to 3/8	0.0020	0.0006	0.0022	0.0009	0.0019	0.0005	0.0021	0.0008	0.0018	0.0005	0.0020	0.0006
3/8 to 5/8	0.0018	0.0004	0.0020	0.0007	0.0017	0.0004	0.0019	0.0006	0.0016	0.0004	0.0018	0.0005
5/8 to 7/8	0.0012	0.0003	0.0013	0.0005	0.0011	0.0003	0.0012	0.0004	0.0010	0.0003	0.0012	0.0003
7/8 to 1 1/4	0.0008	0.0002	0.0011	0.0003	0.0007	0.0002	0.0010	0.0002	0.0007	0.0002	0.0009	0.0002
Finish Forms Widths												
0 to 3/8	0.0018	0.0007	0.0020	0.0008	0.0017	0.0006	0.0018	0.0007	0.0016	0.0005	0.0017	0.0006
3/8 to 5/8	0.0014	0.0005	0.0015	0.0006	0.0013	0.0005	0.0014	0.0006	0.0012	0.0004	0.0013	0.0005
5/8 to 7/8	0.0010	0.0004	0.0012	0.0004	0.0009	0.0004	0.0010	0.0004	0.0008	0.0003	0.0010	0.0003
7/8 to 1 1/4	0.0007	0.0002	0.0009	0.0002	0.0008	0.0002	0.0009	0.0002	0.0007	0.0002	0.0008	0.0002

of instances have been encountered in which various of these grades have been run at speeds far above the maximum shown in the chart. These cannot be considered standard practice or of any but individual interest since they occur in only a relatively few isolated cases. This chart is based upon a conservative estimate of a great number of jobs run on a production basis on all types of machines in many plants.

The chart indicates that the range of speeds over which the various steels may be cut is wider in the leaded group than in the nonleaded. This probably presents an advantage to the producer of certain parts where special requirements in fabrication are necessary. It might also tend to equalize certain limitations in equipment. It cannot, however, be claimed to present any great advantages to the average user.

Examination of the chart seems to give some credence to the claim that lead presents an additive influence to the increase in machinability afforded by sulphur.

An unbiased examination of various data on resulphurized open-hearth screw stocks must lead to the conclusion that melting practice is an operative factor in good machinability. Experience indicates that high silicon fully killed heats are more subject to machining troubles than are those not so fully killed containing less silicon and a coarser McQuaid-Ehn grain size. This situation holds regardless of the presence or absence of lead which is apparently not a powerful enough influence to overcome other factors tending toward poor cutting quality in the steel prior to its introduction. A number of comparative checks have been taken on large production jobs where many different heats of the same grade were applied from time to time on a particular part. It was found that best results were obtained when adequate control was placed on melting practice to produce factors known to make for good machining in S.A.E. analyses. The same control of these factors was found to be necessary in manufacturing lead-bearing heats for the same jobs.

The efforts which have been made to improve machinability have in general illustrated that mechanical means are limited in scope. Much more effective are melting practice and addition of some foreign element or elements which serve primarily to break up free ferrite areas thus fostering a fine and well broken up chip which will clear the tool effectively and prevent the generation of excessive heat. At this point, cost of such an addition becomes an opera-

tive factor not only in regard to the cost of whatever foreign material may be added but extra production costs which arise as a result of such additions. The benefit to the user of such a product is dependent upon his opportunity to regain this extra cost with a margin of saving or gain for himself.

A general rule which governs the selection of a so-called free or exceptionally free machining steel for any given job refers to the proportion of machine work to the gross amount of steel in the part. If this proportion is high the increased cost of such a steel can be justified and will in all but a very few instances reflect a calculable saving in part cost. If the proportion is low, the job will seldom bear an additional cost for free machining properties, if any, and almost never for exceptionally free machining properties. Lead, of course, is governed by this rule as is sulphur.

Other factors naturally enter into the selection of a material which will ultimately reduce the finished part cost to a minimum. Type and age of equipment, machine speeds available and tooling operations involved must be considered. Effort has been made to reduce a comparison of machinability of different types of steels to an index number in various ways. While this method is not to be underestimated, the present writer feels that too many variables enter into machine operation and part fabrication to permit of such a relationship being more than an indication of comparison. The theoretical aspects of machinability and an excellent practical definition of it were discussed very ably by Knowlton (Ref. 8).

He says "the most machinable steel is the one which will permit the fastest removal of the greatest amount of material (before resharpening the tool) with a satisfactory finish."

The following data is evidence of an effort to determine just how lead-bearing steels compare with other types of free machining steels available for production use in meeting this definition.

Practical aspects of the ability of lead-bearing steels to meet the requirements of this definition have been discussed with machine operators, set-up men and others directly concerned with machine operation. Their comments have in many instances been very illuminating. The tendency seems to be a change in fabricating methods determined by individual requirements although in all cases maintenance of most satisfactory part finish seemed to be the predominant influence. Commensurate with this, peripheral speed is increased or tool feeds advanced. On the newer types of equipment

an increase in speeds with no increase in feeds seems to be producing the best results. With this procedure tool life in some cases has shown an enormous increase—as much as 50 to 75 per cent—and from this has tapered down to a point actually less than when run at slower speeds. A measurable increase in tool life is invariably found when running leaded steels at feeds and speeds of nonleaded steels of the same grade. Further, at advanced speeds leaded Bessemer screw stocks maintain their advantage over the leaded open-hearth screw stocks. In connection with part finish it should be mentioned that in the leaded steels, this characteristic is maintained regardless of the tool life experienced.

Examination of tools which have worn to a point where regrinding is necessary shows more of a tendency to wear rather than burn, showing that frictional heat is minimized due presumably to adequate chip clearance. These conditions seem to remain the same regardless of rakes and clearances. No recommendations could be made, therefore, for changing these angles except on open-hearth grades where a slight increase in back rake angle appears advisable. The finely broken up chip serves to make possible a smooth wall or side surface with little or no side clearance.

A factor of considerable interest which is worthy of comment in all grades of steel is the "efficiency of machine operation." This controls directly the net production per hour from a machine and any factors which lessen down time of a machine increase the per cent of gross parts per hour from a machine and thus raise its efficiency. Many operators and set-up men seem to favor running at slower speeds with medium cuts to gain increased production and to lower fabricating costs by increased efficiency of operation in running more minutes per hour. This minimizes wear on the machine, lowers tool cost per unit part, gives longer life on spindles, collets and tool slides. These factors are not capable of being calculated into actual savings, but over a period of time will mount to sizable proportions. One feature that looms large in the operator's opinion is that very fine chips eliminate the necessity of frequent stopping of a machine to clear away the chips which are a frequent cause of annoyance when the chips are long and curly. Salvage of the oil from chips is easier when they are well broken up.

One feature which has been called to attention a number of times is the difference between leaded and nonleaded steels in milling and threading operations. Both operations are being inves-

tigated from every angle and so far no definite results have been brought to light. In individual instances, relief has been obtained by an increase in quality of lubricant and/or by the use of a good quality tool, tap or die. This situation is not found a general complaint and further investigation will doubtless tie it down to individual situations.

Grinding of hardened parts has not shown any differences peculiar to lead bearing steels. Grinding of unhardened leaded steel has infrequently presented a problem of loading the wheels, making frequent dressing necessary. A slightly softer wheel has been found in some cases to eliminate this but is not considered as standard practice unless a definite problem requires solution. A change in lubricant has at times been found beneficial.

From the preceding discussion it must be evident that lead-bearing steels do not present an economic answer to all machining problems nor can they be used for all types of parts. In some parts, such as an agitator shaft, not enough machine work is performed upon the part to justify any added cost for free machining quality which must be paid over the entire shaft. In other cases part fabrication time is already so low that it cannot be cut more without necessitating increased labor costs for restocking the machine or without increased machine upkeep and repair costs.

Table X gives the results of a machine test of four grades of steel, S.A.E. X-1314, 1020, X-1112 and 1115, in comparison with the same type analysis containing lead. The steels were all chosen from production heats and were not selected on any basis other than conformance to analysis specification. They represent, therefore, average production and can be expected to show average expectancy in fabrication.

All the tests were run on the same machine—a Model "K", 6-spindle Cleveland. The bar size was 1½-inch round cold drawn and each test represented six bars.

The section of the table entitled "Inspection" shows the quality of the finished part and must play an active part in the final selection of material for the job. The effect of feeds and speeds upon part quality is illustrated.

The choice of steel on the basis of these data rests upon X-1314 leaded even though other considerations, such as grouping many parts into one steel grade, might influence a final selection to a certain degree in the interests of lower quantity extras, etc. Total

Table X

Steel	Operation	R.P.M.	Feed	S.F. Per M.	Part No. 26627—C. V. Body—1½" Size			Form Tool Average
					Cycle	Allowed Time	Gross Prod. Per Hour	Net Prod. Per Hour	
Test No. 1 X-1314 Lead	Form, Drill, Chfr. Tap and Cut Off ½"—20 Tap, 1" deep—Top size drill 1/16" deep	761	0.004	175'	0.53	20% off grs. prod. for mach. trbl. Change Tools	113	90.4	609 pcs. 1/16" loss on tool per grind
Test No. 2 X-1314 Lead	ditto	843	0.004	193'	0.48	ditto	125	100	ditto
Test No. 3 S.A.E. X-1314	ditto	591	0.0035	136'	0.65	ditto	92	73.6	400 pcs. ditto
Test No. 4 S.A.E.-1020 Lead	ditto	591	0.0035	136'	0.65	ditto	92	73.6	300 pcs. 3/32" loss on tool per grind
Test No. 5 S.A.E.-1020 Lead	ditto	761	0.004	175'	0.53	ditto	113	90.4	No Test
Test No. 6 S.A.E.-1020 Lead	ditto	937	0.0037	205'	0.40	ditto	150	120	No Test
Test No. 7 X-1112 Lead	ditto	937	0.0037	205'	0.40	ditto	150	120	500 pcs. 1/16" loss on tool per grind
Test No. 8 X-1112 Lead	ditto	1044	0.0033	236'	0.32	25% ditto	188	151	400 pcs. ditto
Test No. 9 S.A.E. X-1112	ditto	761	0.004	175'	0.53	20% ditto	113	90.4	500 pcs. ditto
Test No. 10 S.A.E. X-1112	ditto	937	0.0037	205'	0.40	ditto	150	120	No Test
Test No. 11 1115-Lead	ditto	937	0.0037	205'	0.40	ditto	150	120	600 pcs. ditto
Test No. 12 1115-Lead	ditto	1044	0.0033	236'	0.32	25% ditto	188	151	300 pcs. 3/32" loss on tool per grind
Test No. 13 S.A.E. 1115	ditto	591	0.0035	136'	0.65	20% ditto	92	73.6	400 pcs. 1/16" loss on tool per grind
Test No. 14 S.A.E. 1115	ditto	654	0.0035	150'	0.59	25% ditto	102	86.5	300 pcs. estimate only

S.A.E. 1115		ditto	654	0.0035	150'	0.59	25% ditto	102	86.5	per grind 300 pcs. estimate only

Table X—Continued

Steel	Tap Life Average	Cutting Oil	Remarks	Seat of Body	3/8" P.T.	Needle	Material	Labor	Tools	Total Cost Each
Test No. 1 X-1314 Lead	2500 pcs.	Paraffine and cresol Z-2 4% mix	Very good quality thread	X	X	O.K.	0.00938	0.00281	0.00096	$0.01315
Test No. 2 X-1314 Lead	1500	ditto	Fair thread slightly rough would pass	.....	.....	.....	0.00938	0.00254	0.01151	0.01343
Test No. 3 S.A.E. X-1314	2000	ditto	Good quality will pass inspection	O.K.	O.K.	O.K.	0.00902	0.00345	0.00370	0.01617
Test No. 4 S.A.E.-1020 Lead	1000	ditto	Threads rough—doubtful for inspection	O.K.	X	O.K.	0.00890	0.00345	0.00742	0.01977
Test No. 5 S.A.E.-1020 Lead	No test	ditto	Threads rough would not pass	.....	.....	.....	0.00890	0.00281	0.00742	0.01913
Test No. 6 S.A.E.-1020 Lead	No test	ditto	No good threads rough	.....	.....	.....	0.00890	0.00212	0.00742	0.01844
Test No. 7 X-1112 Lead	1500	ditto	Quality threads will pass	X	O.K.	X	0.00914	0.00212	0.00351	0.01477
Test No. 8 X-1112 Lead	1000	ditto	Threads fair would pass	.....	.....	.....	0.00914	0.00168	0.00474	0.01556
Test No. 9 S.A.E. X-1112	1500	ditto	Good thread would pass	X	X	X	0.00878	0.00281	0.00351	0.01510
Test No. 10 S.A.E. X-1112	No test	ditto	Rough threads doubtful	.....	.....	.....	0.00878	0.00212	0.00351	0.01441
Test No. 11 1115-Lead	2000	ditto	Very high quality will pass inspection	O.K.	X	O.K.	0.00914	0.00212	0.00247	0.01373
Test No. 12 1115-Lead	1000	ditto	Threads little rough would pass	.....	.....	.....	0.00914	0.00168	0.00742	0.01824
Test No. 13 S.A.E. 1115	1500	ditto	ditto	O.K.	O.K.	O.K.	0.00878	0.00345	0.00404	0.01627
Test No. 14 S.A.E. 1115	1200	ditto	Threads rough would not pass	.....	.....	.....	0.00878	0.00293	0.00528	0.01699

Table XI

Valve Disk Made from S.A.E. and Leaded X-1335

Bar size 1⅞-inch round
Part length 0.3125 inch, cut off allowance 0.190 inch plus 0.020 inch for facing
Total machine length 0.5225 inch
Steel required to make 10,000 parts 4,091 pounds.

	S.A.E. X-1335	Leaded X-1335
Surface feet per minute	100	150
Time per part in seconds	62	50
Gross production parts per hour	58	72
Net production 80% of gross	46.4	57.6
Hours to complete 10,000 parts	215.5	173.6
Material cost for run	$182.06	$184.11
Labor cost $0.25 per machine hour	53.88	43.40
Machine overhead cost at $1.25 per hour	269.37	217.00
Total cost 10,000 parts	505.31	444.51
Cost per part	0.0505	0.0445

Table XII

Pinion Gear Made from S.A.E. X-1335 and Leaded 1040

Bar size 2⅛-inch round
Part length 1¾ inches with ⅛ inch cut off allowance
Total machine length 1⅞ inches
Steel required to make 6000 parts 11,500 pounds.

	S.A.E. X-1335	Leaded 1040
Surface feet per minute	130	160
Time per part in seconds	22	17
Gross production parts per hour	163.6	211.7
Net production 80% of gross	130.8	169.4
Hours to complete 6000 parts	45.8	35.5
Material cost for run	$463.45	$451.95
Labor cost $0.30 per machine hour	13.74	10.65
Machine overhead cost $1.25 per hour	57.25	44.38
Total cost 6000 parts	534.44	506.98
Cost per part	0.0891	0.0845

part cost of leaded X-1314 is less even though original steel cost is the greatest. Test No. 1 in this grade illustrates further that a lower net production of 90.4 parts per hour results in a material saving in tool cost per part even though the steel could be run to produce a net 100 parts per hour, as illustrated in Test No. 2. Most parts per hour does not result in the cheapest parts.

An examination of all tests results in Table X will show that in each grade the leaded steel shows the best quality parts and the lower cost per finished part. It also shows that while the leaded steel can be run at excessive speeds, Tests No. 2, 8 and 12, the tool cost is increased a great deal at the high rate.

Tables XI and XII present a record of production test runs of leaded and nonleaded steels.

Conclusion

An impartial examination of the data presented and a consideration of general experience with steels such as those reported on, to which small additions of lead have been made for improvement of machinability, must indicate that leaded steels merit a place in the group of steels now available for production purposes. This type of material does present an opportunity for substantial savings in fabrication costs without sacrifice in mechanical dependability.

Recognizing the fact that this type of steel is relatively new, it is to be expected that some of the details of manufacturing procedure have not at times been satisfactorily controlled to develop the best characteristics in the steel. Widening of experience will doubtless result in constant improvement in quality.

Continued investigation of this material for individual use will result in the development of a wider field of application.

Acknowledgment

The hearty co-operation and assistance of the Technical Staff of Bliss and Laughlin, Incorporated, is gratefully acknowledged.

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DISCUSSION

Written Discussion: By E. F. Davis, metallurgist, Warner Gear Div., Borg-Warner Corp., Muncie, Ind.

We are very grateful for the privilege of commenting on the excellent paper on leaded steels by Messrs. Robbins and Caskey.

It is a well known fact that the extremely fibrous types of steel are the poorest in machining properties, and any substance nonabrasive in characteristics which can be incorporated into the steel matrix is beneficial to machin-

ability. When steel is extremely pure and free from nonmetallics, its machinability is inferior. On the other hand, the steels which are dirty from a cleanliness rating with inclusions, such as manganese sulphides and phosphides, are much freer in their cutting properties.

It is obvious, therefore, that the addition of lead, being a soft weak plastic metal, would serve a similar purpose in breaking up the continuity of the ferrite.

Lead does not enter into the phenomena of allotropic steel changes resulting from heat treatment. It does not alloy with the steel and has no reactions with the steel. Areas surrounding a lead inclusion are not decarburized nor differ in structure than the unaffected areas. It elongates with the rolling and does not seem to change its properties. It is still lead suspended in mechanical diffusion.

To attain its maximum effectiveness, it is obvious that the lead must be in an extremely fine particle division and evenly distributed. When this occurs leaded steels do, without question, improve machinability. However, much of this steel in the market has not even had the lead reasonably distributed. There have been large segregates and often considerable areas where no lead has been present. If a machine is speeded up to show a justified economy and some bars have practically no lead in them, the machine produces rough work and much tool trouble; and the operator soon becomes sour to leaded steel. No doubt this has been due to faulty steel-making and the source not being properly set up to produce it; but the buyer is the victim nevertheless.

There is also much opposition to its manufacture by the steel industry for it is claimed the extra $2.00 per ton does not pay for the additional chipping cost and the difficulties attending the incorporation of lead. Also, there is an industrial health hazard common to all metallurgical operations where lead fumes are involved.

Written Discussion: By W. H. Swanger, metallurgist, National Bureau of Standards, Washington, D. C.

The factual data on physical properties and machinability of leaded steels presented in this paper constitute a welcome addition to the published literature on the subject. This paper, and previous ones cited by the authors, have shown the improvement in machinability that may be secured by additions of lead to steels. The form in which the lead is present in steel has not been positively identified in these papers, however, and consequently the mechanism by which the observed improvements are obtained has not been explained.

Earlier discussions on the distribution of lead in steels postulated a submicroscopic state of division or "emulsification" of the lead to account for the lead that was believed not to be visible in the microstructure. This postulate appears to be incompatible with the observed lack of significant changes in physical properties, other than machinability. If the breaking-up of the chips, Fig. 18, resulted from submicroscopic dispersion of lead, it would be expected that the brittleness shown in these chips would be reflected in lowered ductility and impact strength of leaded steels, a result not found by the authors. Formation of an insoluble constituent in a state of submicroscopic division is considered the basis of the age-hardening process. Some effect,

either a strengthening or a weakening, would be expected from a similar distribution of insoluble lead in steel.

The authors apparently do not subscribe to the postulated submicroscopic distribution of lead, as it is not mentioned in the paper. Their micrographs, Figs. 8, 9 and 10, show that at least some of the lead is associated with the sulphide inclusions normally found in steels of this type, without lead. The chart, Fig. 16, shows that the greatest improvement in machinability is secured in the steels classed as free machining without lead. If the improvement in machinability were the result of submicroscopic division of the lead, the improvement should be of approximately the same magnitude in all steels.

It is possible, therefore, that the lead, through association with the sulphide inclusions, increases the effects of the latter in providing free machining qualities. If this association involves formation of lead sulphide, it is to be noted that it would require slightly less than 0.04 per cent sulphur to combine with the usual 0.25 per cent lead in the leaded steels.

The further discussion of the distribution of lead in steels, mentioned by the authors as now in preparation, is awaited with interest.

Written Discussion: By W. E. Bancroft, metallurgist, Pratt & Whitney Division, Niles-Bement-Pond Co., Hartford, Conn.

In this paper the authors have presented a satisfactory amount of data and evidence on the behavior of lead-bearing steels which serves to place increased emphasis on the importance of this material to the metal working industry.

It is evident that lead-bearing steels when properly manufactured can be relied upon to lower manufacturing costs on certain jobs without any sacrifice in quality. I believe it also might have been shown that in other cases an improvement in physical properties could be obtained with no sacrifice in manufacturing cost. For instance, I believe the addition of lead to S.A.E. 1112 steel will not lower the physical properties, especially the ductility, as much as will the addition of extra amounts of sulphur, and since the authors' machine chart shows leaded S.A.E. 1112 steel to be comparable to X1112 in machinability a substitution of lead for sulphur here will result in improved properties with a maintenance of very excellent machinability, and no additional cost.

In the matter of inclusions, Fig. 7 showing the globules of lead squeezed out during carburizing, presents an interesting study. The authors state that these are unusually large segregations resulting from poor mill practice, and that properly melted steel will contain such small finely divided particles of lead that this condition will not take place. It would be interesting to know whether it is possible to determine by means of some simple test applied to the raw bars whether or not inclusions large enough to be harmful are present. For instance, would the macro etch test distinguish harmful segregations of lead, or if the microscope is used can lead be distinguished from sulphides or other types of inclusions?

The comments on the type of chips formed in leaded steels are interesting and important. In most open types of machining the small, well-broken-up chips are undoubtedly an advantage as the authors state, but in tapping I

believe a different condition exists. We know of two or three actual cases where tapping difficulty in leaded steels was overcome by changing the design of taps so as to prevent the small, finely-divided chips from loading and causing binding.

We also know of some work which is being done on the thread milling of unhardened lead screws made of leaded S.A.E. X1335 steel. This work is still quite experimental and has not yet proceeded far enough to be conclusive. However, the evidence so far obtained indicates that leaded X1335 can be substituted for S.A.E. X1320 steel with no sacrifice in machinability. While the maximum in feeds and speeds has not yet been reached the results so far show that surface finish and cutter life are about equal, and distortion during machining which is one of the big problems in this operation is no worse with leaded X1335, provided the steel has been properly processed in the bar form. This will be another case where improvement in strength and wear resistance can be obtained with the only increase in cost being the differential in the price of these two steels.

Written Discussion: By Thomas J. Dolan, assistant professor of theoretical and applied mechanics, University of Illinois, Urbana, Ill.

The authors are to be commended for their frank discussion of the relative machinability and physical properties of leaded and nonleaded steels.

Along with the need for free-machining, low-carbon steels such as screw stock has come the development of many products which are subjected to severe service conditions that create a demand for increased strength of materials. Thus there is a definite need for a steel of greater carbon content than the commonly used screw stocks, but which can be readily machined, and which can be heat treated to obtain high strength or hardness without the necessity of case carburizing. Most of the data included in the paper deal with the relatively low-carbon, free-machining steels.

Many of the data available on leaded steels indicate that perhaps medium carbon or alloy steels containing lead might be substituted for some of the commonly used screw stocks without materially changing the machinability, and with a marked increase in the strength of the finished part. This observation is in line with the trend of the data shown in Fig. 16 of the paper.

The writer has supervised a series of tests in which the ordinary static, repeated load, and Charpy impact physical properties of a leaded S.A.E. 1045 steel were determined, and a measure of the relative machinability was obtained. A comparison of a few of the results with the authors' data for the same steel may be of interest.

The following table of physical properties obtained for the leaded S.A.E. 1045 steel quenched in oil from 1520 degrees Fahr. and tempered at 650 degrees Fahr. is of interest in comparison with the authors' Fig. 12:

Ultimate strength, pounds per square inch	127,000
Yield point, pounds per square inch	90,100
Brinell Hardness No.	248
Per cent elongation (in 2 inches)	18.0
Per cent reduction of area (½-inch diameter specimen)	35.6
Charpy impact strength, ft.-lb.	18.9
Endurance limit (polished specimen in reversed bending) pounds per square inch	63,000
Endurance limit (specimen with small transverse drilled hole) pounds per square inch	20,000

These values compare closely with the authors' curves for water-quenched steel, tempered at 1000 degrees Fahr., except for the reduction of area, which was approximately 54 per cent in the authors' data. Perhaps the differences in type of heat treatment may account for this discrepancy in the two values.

One item worthy of further study is the relative notch sensitivity of leaded steels when subjected to a service condition involving repeated stresses. Flexural fatigue tests of cylindrical specimens 0.40-inch diameter, with a small transverse drilled hole of 0.04-inch diameter in the test section, gave an endurance limit of only 20,000 pounds per square inch. Thus the factor of stress concentration (ratio of the endurance limit of the specimen without abrupt change of section to that of the specimen with a hole) was 3.15. This factor gives a measure of the relative notch sensitivity of the steel, and the value of 3.15 is somewhat higher than the values commonly obtained for many of the nonleaded steels. However, more data must be obtained before any general conclusions can be drawn. It would be desirable if the authors could add further information on fatigue strength and notch sensitivity.

The term machinability is a relative one and may mean any or all of a variety of qualities or properties such as relative tool life, type of chip formed in cutting, time required to perform a given cutting operation, smoothness of surface finish, etc. No single test has ever been devised which will include the many variables involved and give a complete index of the machinability of a steel. The writer's laboratory tests to determine relative machinability of leaded steel, as compared with that of several other metals, were conducted by drilling ¼-inch holes and observing simultaneous values of torque and thrust on the drill by means of dynamometer readings. The average horsepower required to drill the ¼-inch hole was computed, and the relative machinability was based on this horsepower requirement.

It was found that for two different drilling speeds the leaded S.A.E. 1045 steel, when quenched and tempered, required less power for drilling than did several other steels (S.A.E. 3140 and S.A.E. 2345) of about the same strength and hardness. A nonleaded carbon steel of nearly the same chemical composition but of lower strength and hardness required considerably more power than the leaded 1045. The cold drawn leaded steel showed very nearly the same power requirement as the screw stock material S.A.E. X1112. These observations are in agreement with the authors' Fig. 16, and suggest that lead-containing steels might be commercially machinable at higher strength and hardness levels than some of the lead-free steels. While these horsepower requirements for drilling do not give an infallible index of relative machinability, they do yield additional information on another phase of the problem, and the test results indicated that the addition of lead to S.A.E. 1045 steel produced a definite improvement in the relative machinability without materially impairing the other physical properties of the steel.

Oral Discussion

J. W. HALLEY:[1] This paper is a valuable contribution to the rapidly growing literature on leaded steels.

[1]Metallurgist, Inland Steel Co., Chicago.

The machinability data is particularly worthwhile because the authors have had the opportunity to follow performance in a large number of production shops and their conclusions therefore show what the average operator can expect. Their "Machine Chart" will be of interest to everyone concerned with the cutting of steel.

At Inland we have made a large number of comparison tests of physical properties on steel from adjacent ingots, one with lead and one without. These tests have all shown no appreciable difference in properties resulting from the lead addition. The authors' tests on average production material lead to the same conclusion.

The two examples of aggregate of lead given in the paper may give the impression that this condition is very common. Unfortunately infrequent cases have appeared in the past and it required some time to determine the factors causing bad lead distribution. At the present these factors are well understood and it is not a difficult matter to completely avoid aggregates of lead.

GORDON WILLIAMS:[2] In connection with the effect on the physical properties from the lead addition I would like to ask whether any work has been done regarding the transverse properties. We know that in wrought steels with high sulphur content, longitudinal properties may still be excellent but transverse properties damaged, but it has seemed likely to me that that is the mechanism by which we attain greater machinability; th[illegible]s, by greater brittleness in the transverse direction. We know of cours[illegible]at high sulphur or high phosphorus in a cast steel results in over-all brittlenes[illegible], and in the wrought steel the damage is only transverse.

I wonder whether the authors or anyone else have any data as to effect on transverse impact and ductility caused by the lead additions to a normal low sulphur and low phosphorus S.A.E. steel.

Authors' Reply

The authors wish to express their appreciation of the interest shown by the discussers of this paper and the constructive comments which they have presented. Since leaded steels are a comparatively recent development, any contributions as to their character and behavior are of definite interest and value.

As Mr. Davis points out, the maximum effectiveness of lead in improving machinability is not realized if its distribution is not satisfactory, lead segregation being objectionable from this viewpoint as well as for its detrimental effect on part character, as noted in our paper. The manufacturers of leaded steels recognized these facts and have devoted much time and effort to developing satisfactory methods of production control to produce a consistently satisfactory product. Mr. Halley in his discussion indicates that these efforts have been fruitful and that satisfactory methods of controlling lead distribution have been developed. Based on our own experience in recent months, a general improvement in control of this and other factors affecting the character of leaded steels has been evidenced.

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[2]Metallurgist, testing and research laboratories, Deere & Co., Moline, Ill.

While some steel producers have indicated that the present extra charge made for leaded steels does not adequately cover the added manufacturing costs, there is good reason to believe that with increased experience in producing these grades and an increased volume of production, the manufacturing costs will be lowered. When the idea of making a 0.20 to 0.30 sulphur Bessemer steel was first broached to the hot mills, many said that a material of this type could not be economically and successfully rolled. Yet, today, all mills making Bessemer steels are producing S.A.E. X1112 at a price which makes it attractive to the consumer.

While an industrial health hazard is present in the manufacture of leaded steels and in certain fabricating operations as welding where the steel is exposed to sufficiently high temperatures as to oxidize the lead, there is no such hazard present in the majority of uses to which this type of material is put by the consuming trade.

The subject brought up by Mr. Swanger, relative to the mechanism by which lead improves machinability, was purposely omitted from this paper as foreign to its immediate purpose which was to evaluate the merits of leaded steels for industrial applications. Based on our present knowledge, this is still a rather controversial subject, perhaps not yet entirely explainable in the light of current theories regarding attendant metallurgical phenomena.

There is evidence that lead does associate itself with manganese sulphide although probably not in chemical combination with it but rather as metallic lead (Reference 1). In view of the observed additive influence of lead to increase the machinability afforded by sulphur, it is possible that further research along this line may assist in the development of a satisfactory explanation of the means by which lead improves machinability.

Mr. Bancroft presents some interesting observations on the economics of the industrial application of leaded steels from the viewpoint of the steel consumer. Leaded steels offer great possibilities in improvement of product quality without sacrifice in production. Bessemer screw stock may be replaced by leaded open-hearth screw stock giving parts of increased toughness without decreasing the rate at which the parts are produced. Likewise, leaded plain carbon steels as S.A.E. X1020, 1040, etc., may be used as a means of improving production of parts for which the use of resulphurized steel is considered hazardous.

For the purpose of determining the presence of harmful lead segregation, a sweat test has been found to be generally satisfactory. In this test, a ground section of the material is heated at about 950 degrees Fahr. (above the melting point of lead) preferably in a nonoxidizing atmosphere. The presence of heavy lead segregation will be evidenced by the appearance of numerous heavy lead beads on the surface.

We have not been able to definitely identify lead under microscopic examination except when present in large segregates. This is due to the fact that an entirely satisfactory and reliable etchant has not yet been developed. Several etchants have been tried which will indicate the presence of lead but these do not show the distribution or size of the lead particles. One such etchant is a freshly mixed solution of $NaCrO_4$ in glacial acetic acid, alcohol and water. The lead is evidenced by bright yellow lead chromate stains.

Admittedly, the finely broken chip characteristics of the screw stock grades of leaded steels particularly, while an attraction in the majority of screw machine operations, are actually undesirable for others. In addition to tapping, deep drilling and some threading operations might be noted. Fortunately, in many instances, a change in tool grind or in the cycle of operation will correct the difficulty and permit the use of the leaded steel with the economies which it offers on the other machine operations on the part being produced.

The comments which Mr. Dolan makes relative to the possibilities of using leaded steels of higher carbon content and strength to meet conditions of service exposure of increasing severity, call attention to a field of application which while not stressed in this paper has been of vital interest to many steel users. In many instances, medium carbon leaded steels are being used to replace low carbon screw stocks to insure more serviceable parts and yet without any increase in production costs.

We are especially interested in the test data which Mr. Dolan presents. The difference in the type of heat treatment used together with a probable variation in the hardenability characteristics of the materials involved in tensile tests made by the authors and by Mr. Dolan offer a very possible explanation in the discrepancy in values obtained for reduction of area.

In view of the fact that the authors have not had the opportunity of investigating the relative notch sensitivity of leaded steels, the information given in this connection is welcomed. We trust that Mr. Dolan and others who may be investigating this steel characteristic will be in a position to make their findings generally available as a contribution to the published literature on leaded steels.

In answer to the question which Mr. Williams raises as to the transverse properties of leaded steels, it might be stated that while some transverse tensile tests have been made, the information so far developed is not sufficiently detailed as to warrant publication. However, referring to Tables VI and VII, it will be noted that the tests reported therein do offer some information as to the influence of lead on transverse properties. In these crush tests of piston pin and of bushing, the pins (or bushings) were laid flat on the table of the testing machine and a compression load applied. The stresses thus induced were all normal to the direction of the fibers in the material. Thus, any adverse influence of lead on the transverse properties of the material should be evidenced by a lower crush strength of the part. This was not, however, the case. We have a report of a similar test conducted on heat treated bearing bushings made from leaded 1040 and S.A.E. 1040 steels. In this test, a bearing made of leaded 1040 steel was placed on top of a bearing made from the S.A.E. 1040 with their axes at right angles. In no case was the part made from the leaded steel found inferior in physical properties. In a sense, we consider this form of test a more reliable indication of the influence of lead on transverse properties than transverse tensile or impact tests, which are markedly influenced by center segregation and other variable factors not associated with the presence or absence of lead.

THE PREVENTION OF FLAKES BY HOLDING RAILROAD RAILS AT VARIOUS CONSTANT TEMPERATURES

By R. E. Cramer and E. C. Bast

Abstract

This paper discusses the importance of preventing flakes in steel and the suggestion offered that some rolled or forged products may still contain flakes. Literature on flakes appearing during the past year is reviewed.

Experiments were performed to determine the length of time necessary to hold specimens of 131-pound rails at temperatures of 1100, 900, 700, and 500 degrees Fahr. (595, 480, 370, and 260 degrees Cent.) in order to prevent the formation of flakes in rails rolled from hydrogen-treated ingots. A brief discussion is given of the possible mechanism and causes of flake formation. Conclusions are drawn concerning the experiment.

The Importance of Flake Prevention

So much has been written about flakes that it would seem that a good reason must be offered for another contribution on the subject. That reason might be found in the statement that only within the last four years have flakes been eliminated from railroad rails and rolled steel car wheels which will save the railroads and steel manufacturers a large amount of money per year in the future. It is quite probable that other rolled or forged products still contain flakes which occasionally cause failures and the true cause of which is not recognized as yet. The writers have in mind in particular forged products, especially drop forgings, made from billets containing flakes, where the forging operation does not completely reweld all the flakes in the billets. Any product containing the internal cracks known as flakes, put into severe service, is subject to internal fatigue failures or sudden rupture starting from the high concentration of stress at the edges of the flakes. With the accumu-

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A paper presented before the Twenty-first Annual Convention of the Society held in Chicago, October 23 to 27, 1939. Of the authors, R. E. Cramer is special research assistant professor in engineering materials, and E. C. Bast is test assistant, Engineering Experiment Station, University of Illinois, Urbana, Illinois. Manuscript received June 26, 1939.

lated knowledge now at hand on methods of preventing flakes there can be no reason for any product containing flakes except that their presence has not been suspected or no investigation has been made and consequently no precautions have been taken to prevent their formation.

In two previous papers (10, 11)[1] the writers have given selected bibliographies on the subject of flakes and hydrogen in steel. In a review of the literature it is necessary to include hydrogen in steel because of the influence of hydrogen in causing flakes as mentioned later in this paper. During the past year six papers on flakes have come to the writers' attention and a larger number on hydrogen in steel. Only a few of the latter give information directly related to the subject of flakes. The tendency of recent research has been to study the effects of melting practice on the absorption of hydrogen and on the production of flakes.

In an editorial abstract (1) in METAL PROGRESS information is given on the effect of hydrogen in producing flakes in 2000 heats of ball bearing steel, indicating that a prolonged refining time increased the number of flakes. Kuba (2) lists five causes of flakes and five methods of avoiding flakes in the melting practice. Chuiko and Lvova (3) state that flake content increases with the humidity of the air, being particularly affected by rain. They also give information on the effect of moisture content of the lime. Matsuyama, Sasakawa and Iki (4) state that flakes are formed not only by hydrogen but by thermal and transformation stresses and point out the effect of chemical composition on the formation of flakes. Sinitsyn (5) gives information on "Flakes in Railroad Tires" and a method of preventing them by holding for several hours at a stress relieving temperature. Ignatou (12) describes methods of minimizing flakes and methods of testing for flakes.

Schwarz (6) discusses the sources of hydrogen in molten steel and methods of preventing hydrogen absorption during open-hearth melting. Widemann (7) concludes that the hydrogen atoms occupy the empty spaces in incomplete atomic lattices. Moressee (8) gives analytical data on the amount of hydrogen given off during pouring and also the percentage remaining in four grades of steel after solidification. Bamford (9) describes the mechanism by which hydrogen builds up internal pressures and produces flakes in steel.

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[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

Experimental Procedure

The experiments herein reported were planned to determine the lengths of time necessary to hold 131-pound rails at temperatures of 1100, 900, 700 and 500 degrees Fahr. (595, 480, 370 and 260 degrees Cent.) to prevent the formation of flakes, or shatter cracks. The term shatter crack has been used generally to designate flakes in railroad rails but because of the more general usage, flakes will be used in this paper. The chemical analysis of the four heats of open-hearth rail steel used are listed in Table I. All ingots from which the rails were rolled were treated with hydrogen by a process previously described (11) to insure that the steel would have a strong tendency to develop flakes. This treatment produced many flakes in the air-cooled or "control specimens" as shown in Table II. In two cases two ingots of the same heat of steel were treated with hydrogen and the second ingots held in the soaking pits at temperatures above the critical range for 9 and 20 hours, respectively, before rolling. This holding of the ingots apparently reduced the number of flakes in the "control specimens" about 25 per cent.

When the hydrogen-treated ingots were rolled into 131-pound rails, 7 to 9 specimens, two feet in length, were cut from the middle rail of the ingot at the hot saws. The specimens were marked with two numbers, the first designating the number of the test or heat.

Table I

Chemical Analysis of the Four Heats of Rail Steel Used in Tests

Test Run	Holding Temperature Degrees Fahr.	Chemical Analysis—Per Cent				
		C	Mn	P	S	Si
9	1100	0.78	0.87	0.015	0.022	0.20
8	900	0.78	0.87	0.015	0.022	0.20
14	900	0.78	0.90	0.013	0.029	0.23
10	700	0.75	0.92	0.018	0.031	0.21
13	700	0.78	0.90	0.013	0.029	0.23
12	500	0.77	0.91	0.014	0.024	0.22

The second number designates the specimen from that ingot and the length of time it was held in the furnace, i. e., No. 0 was cooled in air, No. 1 was held 1 hour in the furnace, etc. One specimen, No. 0, from each ingot was cooled in air outside the mill building,

as a "control specimen" to determine the tendency of that rail to develop flakes. The remaining specimens were cooled on the mill floor to about 25 degrees above the desired holding temperature and then transferred to a gas-fired furnace heated to that temperature. The temperature of the cooling specimens was determined by clamping a thermocouple on one of the specimens. The furnace was held at constant temperature throughout each test and after 1 hour specimen No. 1 was removed from the furnace and cooled in air outside the mill. After 2 hours specimen No. 2 was taken out, etc., until all specimens were removed. Duplicate tests were made at temperatures of 900 and 700 degrees Fahr. (480 and 370 degrees Cent.) and only one test was made at 1100 and 500 degrees Fahr. (595 and 260 degrees Cent.).

Results of Etch Tests of Specimens

The results of etch tests of all specimens held for various lengths of time at four temperatures are given in Table II. The method of etch testing for flakes consisted of sawing a 6-inch length of the head of each rail into three longitudinal slices. These slices were etched about 1 hour in a 50 per cent solution of hot hydrochloric acid and then immersed ½ hour in a hot 10 per cent solution of sodium pyrophosphate to prevent corrosion. The numbers of longitudinal (L) and transverse (T) flakes were counted on one side of the slice containing the most flakes. Fig. 1 shows a typical etched slice.

It will be noted from Table II that flakes were prevented by holding specimens 3 hours at 1100 degrees Fahr. (595 degrees Cent.); 4 hours at 900 degrees Fahr. (480 degrees Cent.); 4 hours at 700 degrees Fahr. (370 degrees Cent.); and 5 hours at 500 degrees Fahr. (260 degrees Cent.). There is a difference of 1 hour between Test 8 and Test 14 held at 900 degrees Fahr. (480 degrees Cent.) which is explained by the less tendency for the rails of Test 14 to develop flakes, as indicated by the number of flakes in the air-cooled or "control specimens." The effectiveness of the hydrogen treatment of the molten steel in producing flakes is shown by the large number of flakes in all air-cooled specimens. The writers are informed that the above tests are in substantial agreement with results to be published soon by H. B. Wishart and A. N. Swanson on rails of 112-pound section.

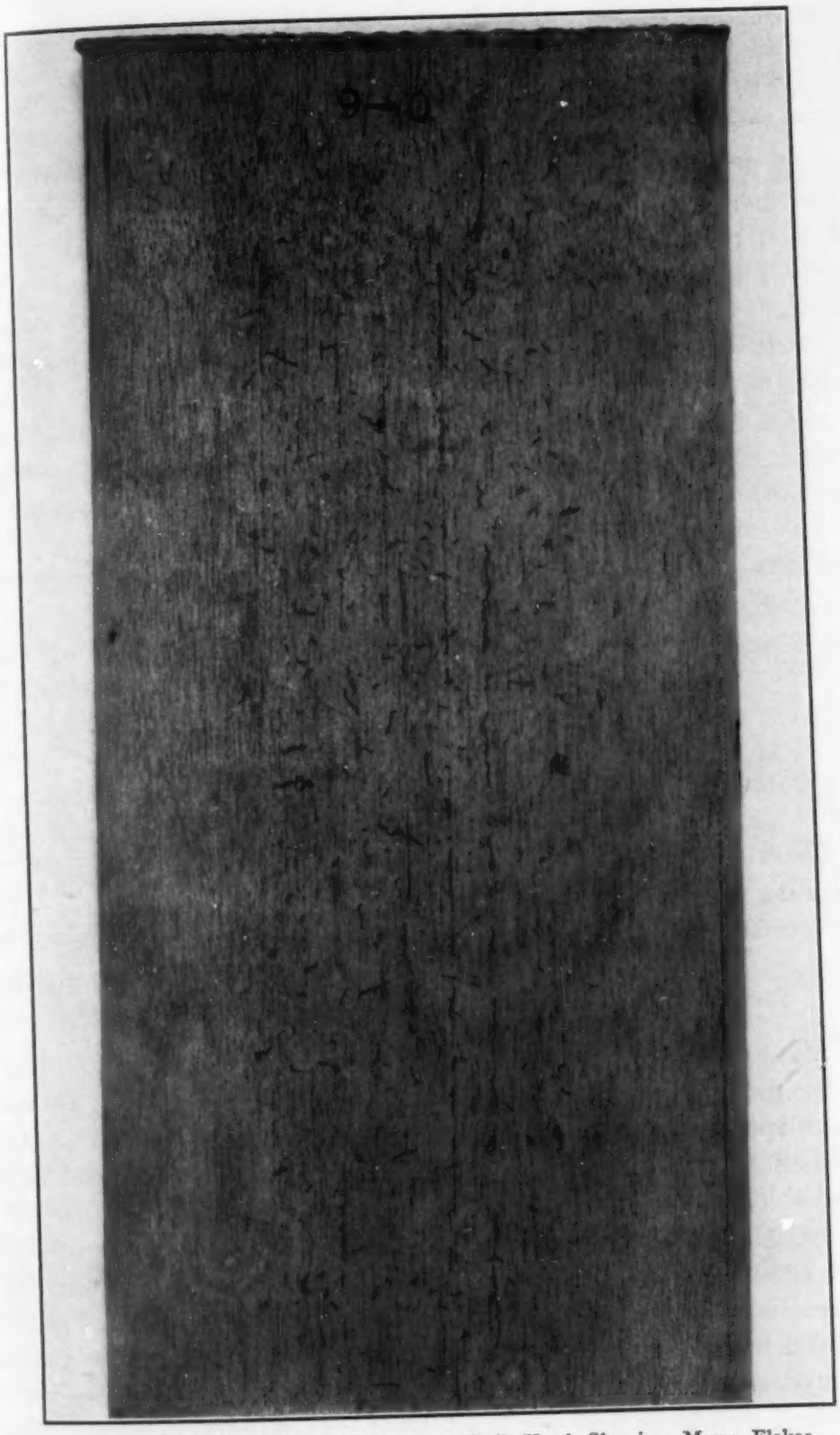


Fig. 1—Typical Etched Slice from Rail Head Showing Many Flakes. × 1. Specimen Not Etched as Deeply as Those Usually Photographed but Gives More Detail of the Flakes. Etched, Hot 5 Per Cent HCl.

Table II
Results of Etch Tests of Specimens Held for Various Lengths of Time at Four Different Temperatures

Specimen No. Test 1	Specimen No. Test 2	Constant Furnace Temperature	Length of Time in Furnace Hours	†Number of Flakes on One Side of 6-Inch Slice Test 1	†Number of Flakes on One Side of 6-Inch Slice Test 2
9–0*	....	Control Spec.	0	105 L, 45 T	
9–1	....	1100° F.	1	65 L, 24 T	
9–2	....	1100° F.	2	5 L,	
9–3	....	1100° F.	3	0	
9–4	....	1100° F.	4	0	
9–5	....	1100° F.	5	0	
9–6	....	1100° F.	6	0	
8–0*	14–0*	Control Spec.	0	160 L, 44 T	87 L, 18 T
8–1	14–1	900° F.	1	86 L, 14 T	26 L, 4 T
8–2	14–2	900° F.	2	55 L, 8 T	8 L,
8–3	14–3	900° F.	3	3 L, 2T	0
8–4	14–4	900° F.	4	0	0
8–5	14–5	900° F.	5	0	0
8–6	14–6	900° F.	6	0	0
10–0*	13–0*	Control Spec.	0	116 L, 19 T	118 L, 21 T
10–1	13–1	700° F.	1	85 L, 8 T	94 L, 10 T
10–2	13–2	700° F.	2	14 L,	29 L, 1 T
10–3	13–3	700° F.	3	1 L,	4 L,
10–4	13–4	700° F.	4	0	0
10–5	13–5	700° F.	5	0	0
10–6	13–6	700° F.	6	0	0
10–7	13–7	700° F.	7	0	0
12–0*		Control Spec.	0	139 L, 46 T	
12–1		500° F.	1	138 L, 57 T	
12–2		500° F.	2	52 L, 28 T	
12–3		500° F.	3	44 L, 5 T	
12–4		500° F.	4	10 L, 1 T	
12–5		500° F.	5	0	
12–6		500° F.	6	0	
12–7		500° F.	7	0	
12–8		500° F.	8	0	

*Control specimen cooled in air outside the mill.
†Flakes are recorded as the number of Longitudinal (L) or Transverse (T) flakes on one side of a longitudinal slice 6 inches long.

The Mechanism and Causes of Flake Formation

Many theories have been advanced as to the causes of flakes and the method by which flakes are developed in steel. The following explanation seems to the writers to agree with most of the printed information. Flakes form in certain heats of high carbon and alloy steels which are finished in bars or billets of rather heavy cross section and allowed to cool to room temperature in a few hours. The flakes slowly begin to develop at temperatures between 300 and 100 degrees Fahr., depending on the amount of hydrogen present in the steel and on the size and rate of cooling of the piece. Some pieces do not develop flakes until cooled to room temperature for several hours and the flakes may not reach their maximum size in any piece until several hours after reaching room temperature.

Among the primary causes of the development of internal cracks in steel is the natural shrinkage of all steel during cooling. The outside shell of a piece cools somewhat faster than the center portion thus taking a size and shape which it attempts to keep and at the same time the strength of the outside layer of steel increases faster than the steel in the center of the piece. As the center of the piece tends to shrink away from the outside shell during the final cooling, stresses are developed in the center of the piece. Ordinarily these stresses are not great enough to crack the steel but in certain heats some additional stress arises which produces cracks. This additional stress, or the second cause of flakes, seems to be internal pressure built up by atomic hydrogen coming out of solution in the steel and collecting as molecular hydrogen in small voids or at points of weakness such as at the surface of inclusions. It is known that the atomic hydrogen atom is small enough to diffuse through the steel lattice, while after two atoms of atomic hydrogen form a hydrogen molecule, the latter is considered to be too large to diffuse through the steel. Theoretical calculations have indicated that very high stresses could be developed in this manner. Therefore the combination of cooling stresses and internal pressure seems to be a sufficient explanation of flake formation.

This mechanism of flake formation offers some explanation of why flakes do not form within one-half inch or more of the surface of the piece. It also explains why slow, gradual cooling, or holding for a period of time at a constant temperature, allows enough of the hydrogen to escape through the surface of the piece or relieves internal stresses to such an extent that cracks are not produced in the final cooling in air.

Conclusion

The following conclusion can be made as a result of the experiment. For the 131-pound rails used in these tests the formation of flakes was prevented by holding the specimens 3 hours at 1100 degrees Fahr. (595 degrees Cent.); 4 hours at 900 and 700 degrees Fahr. (480 and 370 degrees Cent.); and 5 hours at 500 degrees Fahr. (260 degrees Cent.).

Acknowledgments

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American Railroads—Rail Committee, Mr. J. V. Neubert, Chairman, and the Rail Manufacturers Technical Committee, Mr. F. W. Wood, Chairman. These tests were made under the direction of Professors H. F. Moore and H. R. Thomas of the staff of the Engineering Experiment Station of the University of Illinois. The generous co-operation of the mill executives and members of the metallurgy division and mill superintendents of the Gary Works of the Carnegie-Illinois Steel Corporation, Gary, Indiana, made it possible to obtain the specimens. The writers wish to express their appreciation to all the above mentioned for their help.

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DISCUSSION

Written Discussion: By E. V. Crane, E. W. Bliss Co., Brooklyn, N. Y.

The authors' clear and interesting discussion of the theory regarding the freeing of atomic hydrogen from solution in the crystal structure and its combination into molecular hydrogen with attendant development of internal pressure would seem to the writer to apply to, and to clarify, explanation of the season cracking of brass as in drawn cartridge cases and occasionally similar cracking of stainless steel in the walls of severely drawn shells.

Written Discussion: By C. E. Sims, supervising metallurgist, and C. A. Zapffe, research associate, Battelle Memorial Institute, Columbus, Ohio.

Research of the present type, to obtain quantitative data, is much needed, for in view of the inherent differences in hydrogen content, internal structure and effective chemical forces of other impurities in steel, it is probable that each type of steel and each shape and size of product may require a modified heat treatment for dissociation, re-solution and expulsion of occluded hydrogen. This contention is borne out by the researches of Korber and Mehovar (1)[1] on rail steels, who found that various steel-making processes, analyses and ingot sections responded variously to heat treatment.

Our own investigations (2, 3), however, have led us to place a different order of importance on the various suggested causes of flakes and shatter cracks than the authors of this paper. Hydrogen easily assumes the position of major importance with the others as minor contributors at best.

Metallurgists have been surprisingly slow in accepting hydrogen as a most deleterious element in steel, in spite of the fact that countless experiments and practical observations alike have demonstrated that the strongest steel is amenable to defects caused by this gas (2). It seems that there has been an unnecessary amount of apologizing by writers who find that hydrogen actually does cause flakes, shatter cracks, blisters, spots and similar defects in steel, and as a result many still believe the theory that cooling stresses are largely responsible for flaking. True, cooling stresses may aid in fissuring, but as a primary factor they have been conclusively disqualified (4, 5, 6). Nor is their presence at all necessary for fissuring.

On the other hand, externally applied stresses often provide the "last straw" to actually initiate fissuring in a steel under stress from hydrogen. The accompanying photograph of a broken tensile bar shows an unusual case of flaking. Hydrogen absorbed during an ordinary arc welding procedure has precipitated in discontinuities which, in this particular case, are visible holes, and the radial cracks around these holes can be due to no other cause than the aerostatic stress caused by hydrogen. When the metal ruptured internally to the extent indicated by the surrounding circular area of fine crystals, the pressure of the gas was reduced, tearing stopped and a flake remained. In this case the pressure of the hydrogen was not enough to rupture the steel without aid. When sufficient external stress was applied the flakes formed in a plane perpendicular to the direction of that stress.

The tremendous total pressures of hydrogen that are necessary within a

[1]The figures appearing in parentheses refer to the references appended to this discussion.

cavity to provide equilibrium pressures of atomic hydrogen follow from simple chemical reasons. It is interesting, however, that such occluded hydrogen does



not dissociate, and hence will not re-dissolve below about 800 degrees Cent., and yet defects in steel caused by hydrogen are quite readily relieved at much lower temperatures. An explanation of this apparent anomaly has been proposed elsewhere (*2*).

Written Discussion: By H. B. Wishart, metallurgical laboratory, Carnegie-Illinois Steel Corp., Gary, Ind.

The authors have shown in this paper that it is possible to prevent flake formation in flake-sensitive steel by holding the steel at some temperature between 500 and 1100 degrees Fahr. for a period of time depending upon the holding temperature. The higher the holding temperature, the shorter the holding time required.

The results of tests made on 112-pound rails by Wishart and Swanson* are in general agreement with those of the authors. It was found, however, in the tests with 112-pound rails that holding of the just-rolled and still untransformed steel above the critical temperature was not effective in preventing flakes from forming in the metal when subsequently cooled in air to atmospheric temperature. This indicates that there is a range in which the temperature of the holding process is effective in preventing flakes in steel, the lower limit being above the temperature at which flakes form, and the upper limit being the critical temperature.

We are in agreement with the authors that flakes are caused by a combi-

*H. B. Wishart and A. N. Swanson, "Methods of Preventing Shatter Cracks or Flakes in Carbon Steels," TRANSACTIONS, American Society for Metals, Vol. 27, Sept., 1939, p. 784.

nation of cooling stresses and stresses produced by gas concentration in the steel. We feel, however, that although several methods have been devised to eliminate flaking in semifinished or finished steels, the problem of flake prevention, while old, still remains to be drawn to a satisfactory conclusion. Such a conclusion would be the ability to control the flake sensitivity of the steel as it is being made or before it is hot-worked. This achievement, although possibly beyond attainment, would eliminate the necessity of special handling of steel to prevent flake formation.

Oral Discussion

H. F. Moore:[2] In connection with this paper it may be in order to offer some discussion on the importance of flakes ("shatter cracks") as causing structural damage to rails. Such flakes may be regarded as "stress raisers", causing negligible damage under a few loads, but a potential source of the spreading fracture under many loads commonly called "fatigue" failure. From the mathematical analysis of C. E. Inglis in the *Transactions*, British Institute of Naval Architects, Part I, p. 219, (1913), considering flakes as equivalent to very flat elliptical holes, the theoretical stress concentration would be very high. The localized stress at the edge of the flake might be ten or more times the stress a short distance away. However any such stress causes plastic action and a reduction of the localized stress below its theoretical value. Tests made in the Talbot Laboratory of the University of Illinois indicate that a small crack in a fatigue specimen of rail steel may reduce its resistance to the spread of the crack to a value as low as 50 per cent of the endurance limit of the uncracked steel. From either the theoretical or the practical viewpoint, flakes in rail steel very seriously reduce its resistance to repeated stress.

It has been claimed that flakes in steel are not real cracks, but that they are converted into cracks by the etching process used to detect them. At the University of Illinois shatter cracks were detected by Mr. Cramer in unetched rail steel by the use of a microscope with a magnification of $\times$ 2000. These cracks had a width of the order of magnitude of 0.00001 of an inch. Their width was greatly increased by etching, but not their length.

Authors' Reply

In answer to Mr. Crane's discussion on the season cracking of brass, we hardly think that hydrogen is the cause of this troublesome phenomenon. I believe it is generally considered to be due to atmospheric oxidation along the grain boundaries in highly strained metal. However, like rails, the cracking may be prevented by holding at a suitable temperature. For the formation of shatter cracks in steel we consider that the bar or piece must be of sufficient cross section that the hydrogen will be entrapped at least ½ inch from an outside surface. This is quite a different condition than the development of season cracking in drawn cartridge cases mentioned by Mr. Crane.

We are very pleased to hear that Messrs. Sims and Zapffe have a paper to be published soon on "Flakes, Shatter Cracks and Hydrogen in Steel." We have been working closely with Messrs. Wishart and Swanson on this

[2]Research Professor of Engineering Materials, University of Illinois, Urbana, Ill.

subject and additional workers in the United States are most welcome so we will look forward to reading their paper. We also feel that the effect of hydrogen on steel has been a subject neglected by most American metallurgists and a thorough investigation may lead to information which will explain some of our present obscure metallurgical phenomena. We have in mind the A_0 line in the iron-carbon diagram, which to us looks like it may have some connection with the solubility of hydrogen in iron.

Messrs. Sims and Zapffe state that they place a different order of importance on the causes of flakes than the writers. In our paper we did not intend to rate the order of importance of the causes of flakes but only mentioned cooling stresses first and hydrogen second. Actually we do not know much about the stresses which may exist during the cooling of a bar of large cross section, especially a shape like a railroad rail, and we should remember it is not the stresses left in the cold bar but those which exist during cooling which count. Therefore we would hesitate to say which cause of internal stress is the more important. We do, however, feel that cooling stresses cannot be neglected because experiments have shown that the number of flakes developed in railroad rails can be considerably increased by simply cooling the rail with a mill ventilating fan.

Messrs. Sims and Zapffe mention fissuring in their discussion as a synonymous term for flaking. To those who work with railroad rails the term fissure means an internal fatigue failure starting at a flake. It is hoped the meaning of the two terms will not confuse our metallurgical literature.

I am glad Mr. Wishart brought up the question of the ability to control the flake sensitivity of steel as it is being made or before it is hot-worked. This would certainly be the ideal solution of the flake problem but until that method is discovered controlling the rate of cooling will probably have to be used on millions of tons of rails and other products. One new development which has been applied commercially during the past year is the dehumidification of air for the blast furnace. This should reduce the amount of hydrogen in the molten pig iron but in the open-hearth process a much larger quantity of hydrogen is introduced in the fuel. It looks like someone will have to develop a dehydryzer to add during pouring as deoxidizers are used at present.

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INTRODUCTORY STUDY OF THE NITRIDING OF HARDENED HIGH SPEED STEEL BY THE USE OF MOLTEN CYANIDES

By J. G. Morrison and J. P. Gill

Abstract

This paper treats with considerable detail the process of surface hardening of hardened high speed steel by immersion in a molten cyanide bath. The paper is divided into two main parts, one of which deals with the reactions that take place within the bath during the process and the precautions necessary with the bath to obtain the most satisfactory results. The second part of the paper is a study of the effect of the process on the steel and discusses the amount of nitrogen that is imparted to the surface, the nature of the surface itself, the hardness of the nitrided surface and the microstructure. The paper is intended as an introductory study as the investigation is being carried further.

THE use of molten cyanides for the nitriding of hardened high speed steels is older than is generally recognized. The history of the process is obscure and considering the general application of the process at the present time it is surprising that only brief descriptions of the operation have appeared in print and these in connection with technical literature of an advertising nature.

John Wandersee of the Ford Motor Company, who has had an intimate contact with most of the major developments of steel compositions and treatments of the Twentieth Century, states that in about 1914 Alfred C. Blaich mentioned to him that he had heard that someone in Chicago was treating hardened high speed steel by immersion in molten cyanides. Messrs. Wandersee and Blaich discussed the process with Edwin Peterson who was at that time foreman of the heat treating department of the Ford Motor Company and who is now with the Commercial Steel Treating Company of Detroit, Michigan. During the summer of 1914 Mr. Peterson treated a number of tools as suggested by Mr. Blaich and found the treatment to improve greatly the cutting efficiency of certain types of tools. It,

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therefore, seems that the true originator of the idea is unknown.

It is most difficult to understand why a process of such universal use has lacked intensive study other than the fact that its apparent simplicity did not appear to offer a fertile field for investigation. Today practically every manufacturer of high speed steel tools uses the process to a varying degree and in most instances with considerable benefit to the product.

The process as usually conducted consists of immersing the hardened and tempered tool or the hardened, tempered and ground tool in an aged molten mixture of sodium cyanide and potassium cyanide. The temperature of the salt is usually within the range of from 1000 to 1050 degrees Fahr. and the time of immersion may be from 5 minutes to even 1 hour or more. This results in an extremely shallow case which has a hardness greatly in excess of that of hardened high speed steel. It was early found that the use of freshly prepared mixtures of sodium and potassium cyanide produced tools having very brittle edges but when the same mixture was aged for a considerable length of time it produced tools relatively free from harmful brittleness.

This investigation was prompted by the desire to gain a working conception, not only of what happens to a tool when it is nitrided but also as to how the process should be manipulated to obtain the desired results. To obtain this information it appeared that the investigation should deal first, with a study of the characteristics of the bath and second, with a study of the material that had been nitrided.

The first part of the investigation relates to:

1. The composition of the nitriding bath.
2. The chemical reactions that take place.
3. The aging of the bath.
4. A study of the contamination of the bath, with particular reference to nickel.
5. A study of the galvanic characteristics of the bath.

The second part of the investigation includes:

6. The nitrogen content of the nitrided surfaces.
7. The hardness of the nitrided surfaces.
8. The microstructure.
9. The nature of the surface as regards appearance, etc.

1. *The Composition of the Nitriding Bath.* As first made, the nitriding bath may be prepared by melting 53 per cent sodium cyanide and 47 per cent potassium cyanide by weight. This is the eutectic

Table I

Melting Points of Various Mixtures of Sodium Cyanide (NaCN) and Potassium Cyanide (KCN) in Per Cent by Weight*

NaCN	KCN	Temperature Degrees Fahr.
100.00	0	1042.8
87.2	12.8	1018.4
75.1	24.9	975.2
63.8	36.2	946.4
53.1	46.9	935.6
43.0	57.0	950.0
33.5	66.5	991.4
24.5	75.5	1031.0
15.9	84.1	1072.0
7.8	92.2	1112.0
0	100.0	1151.6

The above table is that for pure salts and will differ somewhat, but only slightly, with the use of commercial salts.

*International Critical Tables, Volume IV, Page 69.

mixture of the two salts and has a melting point of 936 degrees Fahr., as shown in Table I. For practical purposes a new bath is usually made of 60 per cent sodium cyanide and 40 per cent potassium cyanide as this ratio has a melting point quite close to that of the eutectic. As the bath becomes aged the melting point becomes lower than that of the original mixture, due to the increase of the cyanate content. Additions of new salt are usually made in the proportion of 70 per cent sodium cyanide and 30 per cent potassium cyanide in the interests of economy without any apparent change in efficiency or results.

If an aged bath is heated to 1000 degrees Fahr. and then permitted to cool slowly there will occur at approximately 925 degrees Fahr. a separation of one or more constituents; the separation as regards amount will increase as the temperature decreases. This "salting out" may be observed by using a perforated ladle and scooping the salt from the bottom of the bath. Below are given the compositions of the material scooped from the bottom of the molten bath at 950 and 900 degrees Fahr.:

	Per Cent					
	(CN)	(CNO)	(CO_3)	Na	K	Insoluble
950 Degrees Fahr.	17.81	13.63	14.27	Not determined		20.9
900 Degrees Fahr.	11.16	5.97	36.76	33.1	12.86	....

The sludge sample removed at 950 degrees Fahr. shows no indication of a "salting out." The insoluble residue is quite rich in iron and carbon. In the case of the sample removed at 900 degrees Fahr. the white salt layer was mechanically separated from the gray

colored natural bath sludge. The white "salted out" material is essentially carbonate as indicated by analysis. A 60 per cent NaCN-40 per cent KCN mixture will contain 28 per cent sodium and 24 per cent potassium. The small percentage of potassium found in the "salted out" material would indicate that sodium carbonate is probably the least soluble compound. As carbonate is the end product of the normal decomposition of the nitriding salt, its removal from time to time is possible and perhaps desirable. Holding the bath at a temperature of from 850 to 900 degrees Fahr. permits the removal of much of the carbonate by scooping out with a perforated spoon.

The "salting out" of the carbonate as the bath temperature falls below 925 degrees Fahr. naturally causes a change in the composition of the liquid portion. There are given below the compositions of the bath liquid after cooling from 1050 degrees Fahr. and holding at each temperature for 40 minutes before sampling.

Temperature Degrees Fahr.	Per Cent (CN)	(CNO)	(CO_3)
975	25.26	13.26	12.79
925	25.33	13.49	12.80
875	26.64	15.17	10.21
775	28.20	16.10	6.64

The bath composition is practically the same at 975 and 925 degrees Fahr. At 875 degrees Fahr. the cyanide and cyanate contents have increased while the carbonate has decreased. At 775 degrees Fahr. there is an increase of about 3 per cent of cyanide and 3 per cent cyanate with a decrease of about 6 per cent in the carbonate, as compared to the bath composition at 975 degrees Fahr.

The first experiments in this investigation were made using a nitriding bath that had been in daily use for about three years and, therefore, thoroughly aged. The original experiments were made with a furnace of the electrical resistance type and the pot holding the salts had an inside diameter of 10 inches and an inside depth of 20 inches. The pot was made of an alloy containing 35 per cent nickel and 15 per cent chromium, which type of alloy pot was initially used as it had proven most economical for general cyaniding applications. The thermocouple protection tube inside the pot was originally composed of pure nickel.

The experiments with freshly prepared mixtures were conducted in pressed steel pots 8 inches in diameter and 12 inches deep. Throughout this investigation a 60 to 40 ratio of sodium cyanide to

potassium cyanide was maintained in the preparation of new baths or as additions to aged baths.

In the data from the experiments made, using both an aged and a freshly prepared bath, the identity of the bath used is clearly defined by the cyanogen content of the bath which is given in the tables.

The commercial salts used in making and maintaining the nitriding bath have the following approximate analysis:

Commercial Sodium Cyanide	Per Cent	Commercial Potassium Cyanide	Per Cent
NaCN	96.7	KCN	95.8
Na_2CO_3	2.50	K_2CO_3	0.58
NaCl	0.01	KCl	0.75
NaCNO	0.64	KCNO	0.34
NaOH	0.09	KOH	0.12
S	0.0026	Fe	0.06
Fe	nil	Ni	nil
Ni	nil		

Because of the chemical complexity of a nitriding bath an analysis as usually made is reported as percentages of cyanogen (CN), cyanate (CNO) and carbonate (CO_3). It is impractical to determine the percentages of sodium and potassium compounds of each group.

A freshly prepared nitriding mixture composed of 60 per cent NaCN and 40 per cent KCN after the initial fusion (and providing the temperature of the salt has not exceeded 1100 degrees Fahr.) will show a cyanogen content of approximately 45 per cent as compared to a theoretical cyanogen of 47.8 per cent for pure salts. An analysis typical of such a bath newly made is as follows:

	Per Cent
(CN)	45.22
(CNO)	1.14
(CO_3)	1.87

A thoroughly aged bath will be entirely liquid at approximately 925 degrees Fahr. Below this temperature the bath remains liquid to approximately 775 degrees Fahr. but as already mentioned there is a progressive separation of carbonate as the temperature drops below 925 degrees Fahr. which settles to the bottom of the pot.

A nitriding bath originally composed of 60 per cent sodium cyanide and 40 per cent potassium cyanide becomes on aging and through use a rather complex mixture. A bath which has been in use for a reasonable length of time will contain the following if nickel alloy pots are used:

(1) NaCN
(2) KCN
(3) NaCNO
(4) KCNO
(5) Na_2CO_3
(6) K_2CO_3
(7) Small amounts of tungsten
(8) About 0.10 per cent iron
(9) About 0.01 per cent nickel
(10) Free carbon in the nickel-containing sludge adhering to the bottom and sides near bottom of the pot.

The tungsten is probably present as tungstates of sodium and potassium and finds its way into the bath because of the mild attack of the salt on the steel. The tungsten dissolved appears to be that which was in solid solution in the steel as the carbides appear resistant to attack by the molten salt. The chief source of nickel is the pot itself although some contaminating nickel is derived from the nickel thermocouple protection tube. The iron contamination is probably derived from the wall of the pot; from the film of oxide carried into the bath on the surfaces of preheated samples, and from the KCN.

A fairly representative analysis of a thoroughly aged nitriding bath contained in a nickel alloy pot would be as follows:

	Per Cent
(CN)	21.0
K	28.0
Na	20.5
(CO_3)	14.0
(CNO)	16.5
Fe	0.11
Ni	0.0085
Cl	0.30
W	0.10

2. *The Chemical Reactions.* A nitriding bath during use possesses two zones of almost constant chemical activity. One zone is the surface of the bath where it is exposed to the air; the other zone where contact is made with the surface of the immersed high speed steel. At the surface exposed to air the chemical reactions probably are those given below:

(a) $2NaCN + O_2 = 2\ NaCNO$
(b) $4\ NaCNO + 3O_2 = 2\ Na_2CO_3 + 2CO_2 + 4N$
(c) $2\ KCN + O_2 = 2KCNO$
(d) $4\ KCNO + 3O_2 = 2K_2\ CO_3 + 2CO_2 + 4N$

The internal reactions occurring on the steel surface are probably due to or are at least greatly accelerated by, the catalysis of the salt by the steel surfaces. The probable internal reactions are:

(e) $4\ NaCNO \rightarrow Na_2CO_3 + 2NaCN + CO + 2N$
(f) $4\ KCNO \rightarrow K_2CO_3 + 2KCN + CO + 2N$
(g) $2\ CO \rightleftarrows CO_2 + C$
(h) $NaCN + CO_2 \rightarrow CO + NaCNO$
(i) $KCN + CO_2 \rightarrow CO + KCNO$

Reaction (g) may be reversible although its tendency is probably to the right.

3. *The Aging of the Bath.* The aging of a new bath if contained in a pressed steel pot requires considerable time if the temperature of the bath is not permitted to exceed 1100 degrees Fahr. The bath once melted will age through nonuse due to the surface oxidation of the cyanides. A bath contained in a nickel alloy pot appears to age more rapidly than one contained in a pressed steel pot.

A freshly prepared bath composed of 60 per cent NaCN and 40 per cent KCN contained in an 8-inch diameter by 12-inch pressed steel pot was heated the first, second, fifth and thirteenth days to 1050 degrees Fahr. and held 2 hours at heat each time. Between each heating the bath was covered with a sheet metal cover. On the thirteenth day the cyanate content had increased from 1.03 per cent of the first day to 1.93 per cent. On the fourteenth day the bath was heated to 1300 degrees Fahr., cooled to 1050 degrees Fahr. and held 2 hours at this temperature. The cyanate increased to 2.74 per cent as compared to 1.93 per cent for the previous day. The higher temperature appears to accelerate the formation of cyanate although too high a temperature results in a further decomposition of cyanate.

A 70 per cent NaCN, 30 per cent KCN bath aged in a nickel alloy bath was found to contain over 9 per cent cyanate after aging at 1050 degrees Fahr. for 12 hours.

When a nitriding bath is first prepared the vapor is quite irritating to the nostrils. At this point good ventilation is desirable. When the bath has become aged sufficiently or when it contains a cyanate (CNO) content over 6 per cent there is no appreciable annoyance due to the vapor.

Occasionally an aged bath heated in an electric pot furnace will "blow" rather violently during the "heating up" period, or when the lower part becomes molten and while the top crust remains. This may be of sufficient violence to send the liquid salt a considerable distance. As cyanide burns are quite painful and difficult to heal, provision should be made for a tight fitting cover. A more fool-proof recourse is to add a split sheet metal hood attached to the top of the

furnace shell, and the additional precaution taken that the hood is not raised until the recorder indicates that the salt is melted. Sometimes a steel rod is placed along the inside of the pot, the object being to have the rod transmit sufficient heat to the top crust to soften or melt part of it early enough to release the pressure developed beneath. This recourse, however, does not appear to reduce the "blowing" to an appreciable extent.

A tapered steel or cast iron plug is sometimes placed in the molten bath so that it reaches to the bottom of the pot. After the salt has frozen, the tapered plug is removed by tapping with a hammer. This leaves a well through which the expanding gases may pass. The disadvantage of using a tapered plug is that it is frequently difficult to remove.

The most practicable method is to use a secondary cover consisting of two circular pieces of sheet metal between which is placed ½ to ¾ inch of an asbestos wall board. This cover having three lugs is placed on the inside of the top of the pot clearing the molten salt level by 1 inch and not interfering with the regular pot cover. This added insulation permits the top crust to soften early enough so that it offers little resistance to the expanding gases.

4. *A Study of the Contamination of the Bath with Particular Reference to Nickel.* As has already been mentioned the original work in connection with this investigation involved the use of a container for the molten salts which contained about 35 per cent nickel and a thermocouple protection tube of pure nickel. When it was learned that the bath had become contaminated with nickel and that there was evidence that such a contamination was affecting to some degree the transfer of the nitrogen from the bath to the steel, it appeared desirable to repeat much of the original work but using a bath free of nickel. In reporting the results of these investigations it will be stated in the tables or diagrams as to whether or not the bath was nickel contaminated.

The change to the use of a nickel-free bath was accompanied by a marked general improvement. It was found that the loosely adherent brownish-black deposit which was adhering to the surface of nitrided samples that had been cooled in air from the bath was freed from the surface more readily in washing; that the amount of the surface deposit was materially lessened and that the bath remained at a more constant composition as regards the cyanogen content, the rate of decomposition appearing to be reduced. The latter may be

attributed to the reaction between the salt and the pressed steel pot as probably being less than that between the salt and the nickel alloy pot and lastly the surfaces of nitrided specimens were, after cleaning, a steely, metallic lustre instead of a dull gray lustre. There is ample evidence that nickel was plating on the surface of the specimens when the bath was nickel contaminated. It is quite obvious that such an effect would result in inconsistencies.

Numerous analyses of the nitriding salt were made from time to time. Some thirty determinations were made at various times and the nickel content found to be a relatively constant amount. Using 10-gram analytical samples the nickel contained in the bath was found to analyze between 0.008 and 0.011 per cent with the average being 0.0085 per cent. Analyzing the bath prior to nitriding and again after nitriding a considerable amount of high speed steel the nickel content showed no change in concentration. Below are listed a few determinations of nickel and iron which illustrate the relative constancy of the nickel:

		Per Cent Iron	Per Cent Nickel
(a)	After an overnight shutdown	0.12	0.0089
(b)	After another overnight shutdown	0.11	0.0081
(c)	After another overnight shutdown, the bath stirred and allowed to settle 10 minutes before sampling	....	0.011
(d)	Same as (c) after 4 hours, considerable work having been processed	....	0.011

A nickel alloy pot removed after several years' service was scraped on the inside wall near the bottom and the gray friable material collected. An analysis of this gray-black scale-like material loosely adhering to the sides near the bottom of the pot showed the following analysis after washing a number of times in distilled water to the absence of (CN) as indicated by the silver nitrate test.

	Per Cent
Nickel	29.11
Carbon	9.21
Nitrogen	0.226

Alloy pots used for containers for the cyanide salts fail due to the attack of the molten salt on the interior of the pot on the bottom and sides near the bottom. Any discontinuity such as a loose area of metal is particularly susceptible to attack by the salt. This is also true of thermocouple protection tubes which are welded on the closed end.

The chief source of nickel contamination is the nickel alloy pot. Substituting an iron thermocouple protection tube for the nickel tube showed no change in the nickel concentration of the bath. Substituting a pressed steel pot for the alloy pot, the residual nickel was plated away so that at the end of four days the bath was free from nickel. Retaining the pressed steel pot but replacing the iron thermocouple protection tube with a nickel tube the bath again became contaminated with nickel. Analysis of the bath under these conditions showed the presence of nickel (after several overnight shutdowns) to the extent of 0.007 per cent. During use this nickel plated away faster than it could be supplied from the tube surface so that at the end of an hour or so the nickel concentration dropped to 0.0015 per cent on a 25-gram sample.

Perforated steel baskets used as containers for tools during nitriding become encrusted with a plate of nickel if the bath is so contaminated. The baskets show no tendency to rust due to the protective coat of nickel.

5. *A Study of the Galvanic Characteristics of the Bath.* In studying the changes in weight of samples after being subjected to the nitriding bath, certain inconsistencies were observed which caused an investigation of the galvanic action which was taking place between the bath, the pot and the samples.

A ⅜ x 1 x 4-inch sample of high speed steel was attached to $\frac{1}{32}$-inch diameter soft iron wire and suspended in the bath from a glass around which the wire was wrapped several times. From the glass insulating rod the wire was led to a millivoltmeter and from the millivoltmeter the circuit was continued to the nitriding pot. When the sample was dropped into the nitriding bath there was a negative deflection indicating the immersed sample to be anodic; then a rapid reverse to a positive peak polarity and a continued and rapid drop in voltage to about 9 millivolts which remained nearly constant for the remaining 30 minutes of the test. Numerous other tests were conducted and all indicated the same galvanic pattern, viz.: a negative polarity on immersion indicating the sample to be anodic, a variable but rapid recovery to a relatively high positive polarity in which the immersed sample became the cathode, and then a decreasingly rapid drop in millivoltage to an approximate constant positive millivoltage.

Two samples ⅜ x 1 x ½ inch were polished on all six sides down to "0" metallographic paper and all six sides were passed over

a canvas polishing wheel. The corners were also touched on the canvas wheel to a slight rounding after which the samples were dried and weighed. Both samples were placed in the nitriding bath at the same time. Sample No. 105 was insulated by suspending from a glass rod by means of $\frac{1}{32}$-inch soft iron wire, while sample No. 107 was immersed to the same level in the bath and the iron wire attached to the glass rod but the end of the wire led to a galvanometer placed in the circuit with the pot. The samples were nitrided at 1050 degrees Fahr. for 4 hours.

When sample No. 107 was immersed there was a negative galvanometer deflection then a quick reversal to a positive deflection as the samples increased in temperature. The maximum deflection was 27.5 millivolts; then in 3 minutes the deflection dropped to 9 millivolts; in 5 minutes to 8 millivolts and in 12 minutes to 6.5 millivolts.

The sample was moved up and down in the bath several times and the following readings were observed:

		Millivolts
35 min.	—Deflection—	6.0
1 hr.	—Deflection—	4.25
1½ hrs.	—Deflection—	4.0
2 hrs.	—Deflection—	5.0
2½ hrs.	—Deflection—	4.75
3 hrs.	—Deflection—	4.0
3½ hrs.	—Deflection—	4.5
4 hrs.	—Deflection—	4.0

The change in weights due to nitriding were as follows:

	Before Nitriding	After Nitriding and Scrubbing Surface	Change in Weight
No. 105 (Insulated)	23.9099 gms.	23.9085	0.0014 gms.
No. 107 (Not Insulated)	23.4501 gms.	23.4424	0.0077 gms.

From the above it will be seen that the immersed sample, as soon as it reached the bath temperature, remained cathodic throughout the duration of the 4-hour test. The weight change due to nitriding of the insulated sample No. 105 was considerably less than that of the noninsulated sample No. 107.

After the above experiment, a series of treated high speed steel samples (0.287 x 0.952 x 2.191 inches) were carefully prepared and nitrided in pairs (one sample electrically insulated and the other not insulated) for 32 minutes. Each sample was suspended in the bath to the same depth by means of a $\frac{1}{32}$-inch soft steel wire attached to a glass rod. The wire of the noninsulated sample was led to a gal-

Table II

Change in Weight of Rectangular Samples (0.287x2.191x0.952 Inch) Nitrided in a Bath Free from Nickel Contamination. Electrically Insulated and Noninsulated Samples Compared. Samples Not Preheated Before Nitriding

No.	Nitriding 32 Min.	Per Cent (CN) of Bath	Weights Before Nitriding	(Grams) After Nitriding	Net Change in Weight (Grams)	Weight After Scrubbing	Gross Change in Weight (Grams)
W1			84.7506	84.7453	−0.0053	84.7444	−0.0062
*W2	900° F.	25.2	84.7317	84.7271	−0.0046	84.7263	−0.0054
W3			84.8389	84.8346	−0.0043	84.8345	−0.0044
*W4	950° F.	24.6	84.8483	84.8452	−0.0031	84.8451	−0.0032
W5			84.8391	84.8359	−0.0032	84.8347	−0.0044
*W6	1000° F.	23.2	84.8423	84.8406	−0.0017	84.8402	−0.0021
W7			85.0842	85.0834	−0.0008	85.0820	−0.0022
*W8	1050° F.	23.5	84.8671	84.8705	+0.0034	84.8692	+0.0021
W9			84.7484	84.7505	+0.0021	84.7495	+0.0011
*W10	1100° F.	23.5	84.8172	84.8216	+0.0044	84.8203	+0.0031

*Electrically insulated.
Note—The noninsulated samples were in a galvanometer circuit.

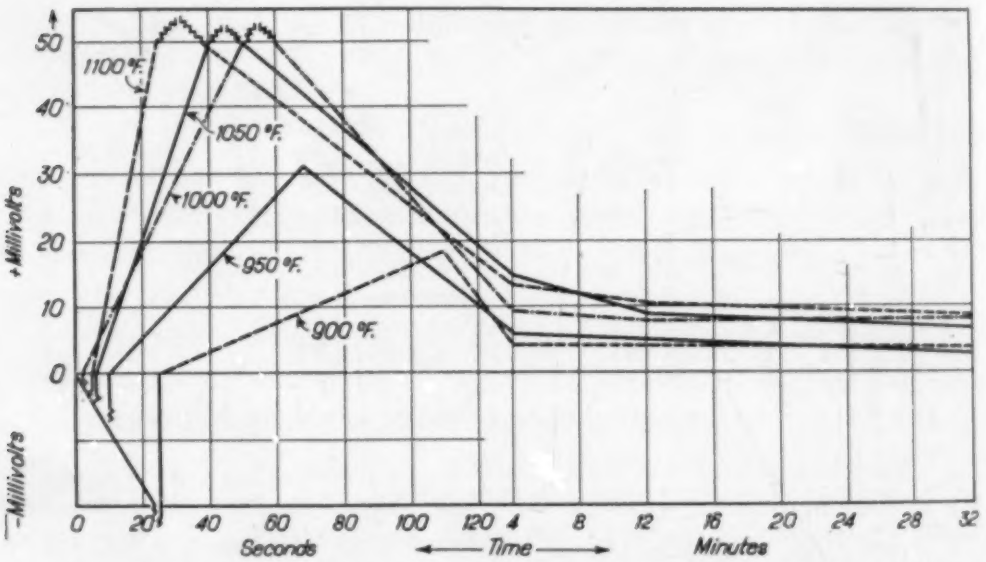


Fig. 1—Galvanic Characteristics of an Aged Nitriding Bath Relative to Samples 0.287 Inch x 0.952 Inch x 2.191 Inch.

vanometer and the circuit completed through the furnace shell. After nitriding, the adherent salt and dark surface deposit was removed from the samples. The samples were then dried and weighed; then scrubbed lightly on all surfaces with emery powder and oil to remove surface smudge and again weighed. Table II shows that the insulated samples lost less weight or gained more weight than the noninsulated samples. Fig. 1 shows roughly the curves that result by plotting the millivoltage against time of immersion, using various nitriding temperatures. The curves of Fig. 1 show that on immersion the sample is anodic but quickly there is a reversal of polarity as the sample

becomes heated, then follows a maximum positive deflection and a gradual drop in millivolts to a near constant. As the temperature of nitriding is increased the maximum positive voltage becomes greater and this millivoltage peak is more rapidly attained.

The foregoing experiment was repeated with samples measuring 0.26 x 2.15 x 0.922 inches. On the noninsulated samples the circuit

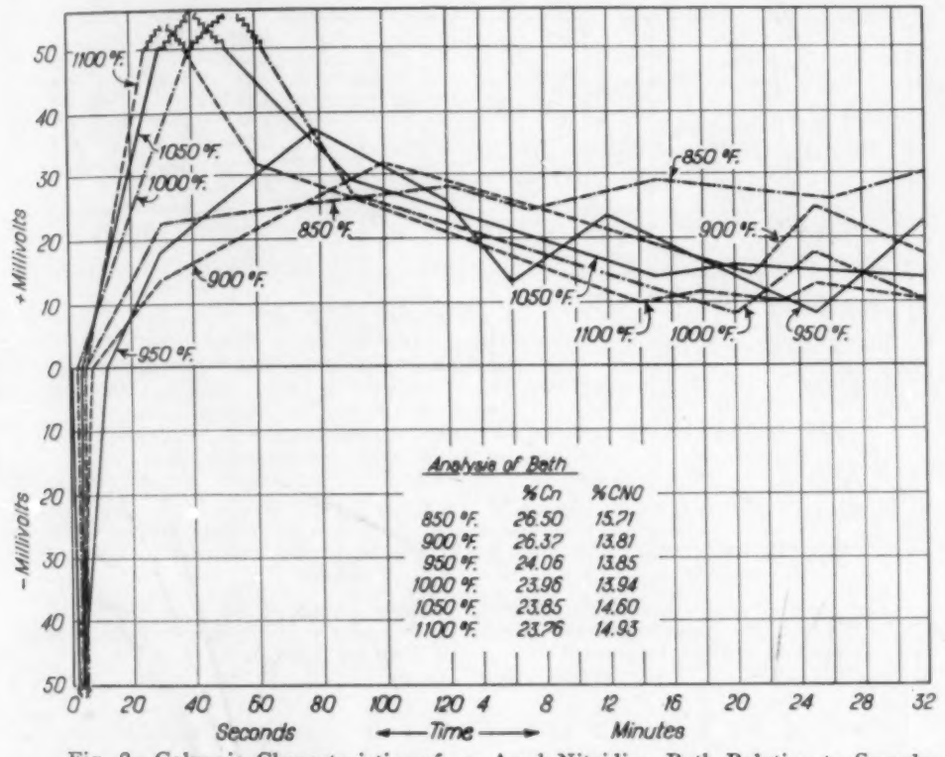


Fig. 2—Galvanic Characteristics of an Aged Nitriding Bath Relative to Samples 0.260 Inch x 0.922 Inch x 2.15 Inch.

was completed through a 3/8-inch diameter rod extension welded to the pot. The use of a double throw switch permitted observations within the range of plus and minus 50 millivolts.

Fig. 2 shows the galvanic curves for the temperatures 850 to 1100 degrees Fahr. in steps of 50 degrees. The curves are given in more detail to show the rise and fall of millivolts. The millivoltage created in immersing a sample in the bath was found to be independent of the electrical heating circuit of the furnace. However, it was found that whenever the furnace was heating there was a rise in millivolts, which was due to the increased circulation of the bath.

Fig. 3 shows the curves developed on the same size samples immersed in a freshly prepared 60-40 mixture. The galvanic characteristics were plotted for the first and succeeding days. The curves

obtained using a fresh mixture show (by comparison with the 1050-degree Fahr. curve of an aged mixture) a low positive peak millivoltage becoming higher on subsequent days as well as attaining the peak more rapidly. On the first day the millivoltage drops quite rapidly to a maintained negative millivoltage. As the cyanate increases the peak voltage rises. On the fourteenth day the cyanate

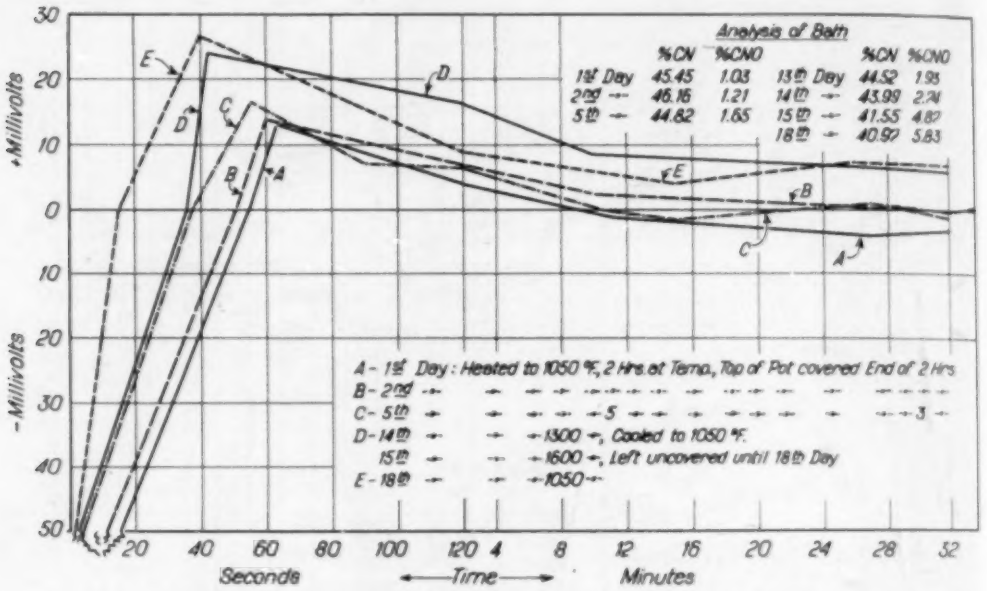


Fig. 3—Galvanic Characteristics of a Freshly Prepared 60 Per Cent NaCn-40 Per Cent KCN Nitriding Bath Relative to Samples 0.260 x 0.922 x 2.15 Inch. Bath Temperature 1050 Degrees Fahr. ± 10 Degrees Fahr.

has increased to 2.74 per cent and a positively maintained millivoltage resulted.

It should be noted that this bath was melted only seven times during the fifteen days. On the thirteenth day the bath was reheated for securing analytical sample only. Between each melting the bath was either covered or left uncovered as noted in the legend of Fig. 3.

It appears that the galvanic characteristics are due chiefly to the decomposition of the cyanate (CNO). The millivoltage is a measure of the decomposition of (CNO) or a measure of the nitrogen created on the surface of the steel. It is also a criterion of a deficiency in (CNO) or a deficiency of nascent nitrogen. The curves obtained on the 850-degree Fahr. sample would indicate considerable decomposition of the (CNO) and consequently a large amount of nitrogen available. However, little is absorbed possibly because of reduced solubility by the steel at the low temperature.

The curves shown in Figs. 1, 2 and 3 illustrate the galvanic

characteristics. The curves are to be considered in only a relative sense since the depth the specimen is immersed in the bath and the location of the specimen in respect to the sides of the pot will influence the millivoltage values. The deeper one places a specimen in a bath or the closer one places it to the wall of the pot the greater the galvanometer deflection. Turbulence or convection currents also influence the millivoltage, particularly in the early period of immersion.

Characteristics of the Product

6. *The Nitrogen Content of the Nitrided Surfaces.* It had been observed that if annealed high speed steel is nitrided it acquired a high degree of hardness on the edges. This hardness on samples immersed for 30 minutes or less at 1050 degrees Fahr. is quite superficial since a file used with ordinary pressure would sink through the case. On a 5-hour immersion at 1050 degrees Fahr. the nitrided case is of sufficient depth and hardness that a more than ordinary file testing pressure is required to break through the case and a high hardness is obvious. It was believed that if one were to nitride annealed high speed steel at various temperatures for various periods of time and remove by machining small increments of the surface layer and analyze them for nitrogen it would show a relatively accurate estimation of the nitrogen absorbed by treated high speed steel. Some comparisons were made of the nitrogen content near the surface between samples of high speed steel that were annealed and samples which were fully hardened and tempered. The amount of nitrogen found present did not differ materially between the nitrogen absorbed by annealed high speed steel and that absorbed by hardened and tempered high speed steel.

Each table clearly shows the type of bath that was used in the experiments as well as to whether or not a nickel or iron pot had been used and as to whether or not the bath was nickel contaminated. The initial test for the determination of nitrogen near the surface was conducted with specimens ¾ inch in diameter and 5 inches in length which had been turned from 1-inch diameter specimens and which had been ground before nitriding.

The steel selected for this test was of the following composition:

C	Mn	P	S	Si	Cr	Ni	V	W
0.70	0.21	0.021	tr.	0.28	4.0	0.078	1.01	18.0

Table III

The Nitrogen Content Near the Surface of ¾-Inch Diameter Specimens, Using an Aged Bath and Nickel Alloy Pot. The Bath Showed Nickel Contamination

Sample Number	Time Nitrided at 1050° F. Minutes	Cyanogen (CN) Content of Bath Per Cent	Percentage of Nitrogen — Depth of Cuts — 0.000 to 0.003 Inch	Percentage of Nitrogen — Depth of Cuts — 0.003 to 0.006 Inch
P1	3	21.4	0.030	0.007
P2	10		0.041	0.008
P3	30		0.059	0.007
P4	90		0.095	0.007
P5	None		Nil	.....

Four annealed high speed steel samples were preheated in a perforated steel basket at 1025 degrees Fahr. and the basket containing the samples transferred to the nitriding bath at 1050 degrees Fahr. The bars were held in the bath for various times. The samples after removal from the bath were cooled in still air and the adherent salt removed by washing in water and by scrubbing of the surface by means of a fiber brush. A fifth bar was not nitrided.

Two successive cuts of 0.003 inch were taken on the nitrided bars and the chips analyzed for nitrogen. From bar P5 which was not nitrided only one cut was taken for the nitrogen content of the steel itself. Regular high speed steel tool bits were used in machining the bars for the analytical samples.

All of the nitrogen determinations were made by the Battelle Memorial Institute following the analytical procedure given in the appendix. Table III gives the history of the various bars and the results of the nitrogen determinations. The results obtained in Table III indicate a progressive absorption of nitrogen as the time of immersion is increased from 3 minutes to 90 minutes; also practically all of the nitrogen absorbed is within the first 0.003-inch depth.

Following this preliminary test for nitrogen it was decided to prepare a number of samples in an effort to determine the nitrogen in samples of cuts 0.001 inch in depth and by difference the amount in the first 0.0005 inch by grinding of 0.0005 inch of surface of companion bars and then taking cuts of 0.001 inch. A larger diameter test specimen was selected in order that the 0.001-inch cuts would yield sufficient chips for a reliable nitrogen determination; also a larger diameter bar would probably show less runout or distortion during nitriding.

For this test 1⅞-inch diameter high speed steel of the following composition was used:

C	Mn	P	S	Si	Cr	Ni	V	W
0.705	0.21	0.018	tr.	0.33	3.98	0.06	1.03	18.16

Samples 5.5 inches long were turned to 1.75-inch diameter and then ground between centers to a good tool room finish. Samples were nitrided at various temperatures for 30 minutes following a preheating period at the same temperatures as that used in nitriding. Cyanogen determinations were made on samples of salt taken from the bath at the time each sample or samples were run at the various temperatures. After cooling in still air the samples were placed in water and the loosely adherent brownish-black deposit removed by brushing with a fiber brush. The samples were then immersed for 5 minutes in cold 25 per cent hydrochloric acid, containing an inhibitor, to remove any possible film of cyanide on the surface.

The test specimens after cleaning showed a more or less uneven dull gray and black surface suggesting surface deposited carbon. The analytical samples were obtained under laboratory supervision, the lathe work and micrometer measurements being done by an expert tool room mechanic. Some estimate of the care exercised in attempting to maintain preciseness of measurement may be gaged by the fact that it required the work of two men for five days to secure the chips of three cuts from each of ten samples.

Several attempts to remove the first 0.001 inch of metal on sample N1 indicated that this was hardly possible of accomplishment with a regular high speed steel tool bit. After this experience tantalum carbide tools were used to machine off the successive cuts.

The following observations in regard to machining the nitrided samples may be of interest in view of the subsequent data obtained on the hardness conferred on annealed high speed steel by nitriding only. Bars N1 to N4 inclusive were machined without difficulty. On bar N5 the tool failed once on the first cut; the second and third cuts were obtained without difficulty. On bar N6 the tool failed seven times in securing the cut of 0.0005 to 0.0015 inch. On bar N7 there was consistent tool failure in attempting to cut the first 0.001 inch. This sample was machined satisfactorily to a depth of 0.002 inch and the chips were quite sooty. On bar N8 it was necessary to go to a depth of 0.002 inch on the first cut. The first 0.001 inch of bar N10 was removed without difficulty, and the chips were

crumbly and sooty, as if they had been virtually ground off by the tool as the bar was glazed entirely across after removal of this first 0.001 inch. There was a consistent tool failure in attempting the second cut of 0.001 to 0.002 inch and also in attempting to cut 0.001 to 0.003 inch. The second cut was finally accomplished in making a cut 0.001 to 0.00475 inch. The chips on the second cut appeared quite dark in color. Bars N13 and N14 machined satisfactorily to 0.001 inch cuts.

The nitrogen determinations listed in Table IV show that practically all of the nitrogen absorbed in the 30-minute immersion periods from 850 to 1150 degrees Fahr. inclusive is within the first 0.001 inch of surface; also, the nitrogen in the second and third 0.001 inch is appreciably greater than that found in the steel itself. Thirty minutes at 1250 degrees Fahr. evidently drives the nitrogen beyond the first 0.001 inch of surface as indicated by our inability to remove the first 0.001 inch by means of a carbide tool.

Table V shows an increasing percentage of nitrogen is obsorbed in an aged bath at 1050 degrees Fahr. as the time of immersion is increased from 3 minutes to 6 hours. Three hours at 1050 degrees Fahr. evidently drives considerable nitrogen to a depth greater than 0.001 inch, precluding removal of the first 0.001 inch with a carbide tool. On sample N10, nitrided at 1050 degrees Fahr. for 6 hours, the first 0.001 inch was removed without difficulty. However, a fortuitous combination of circumstances permitted this. The first 0.001 inch of surface was probably a more or less "built up" surface consisting of carbon, nickel and a steel surface more or less disintegrated with minute pits. The surface of sample N10 after removal of the first 0.001 inch was glazed entirely across. The second 0.001 inch could not be cut with a carbide tool; the attempted cut of 0.001 to 0.003 inch could not be accomplished. The second cut was finally made 0.001 to 0.00475 inch. A penetration of considerable nitrogen to a depth greater than 0.003 inch appears evident.

The nitrogen analysis of sample N14 which was nitrided in a freshly prepared 60-40 mixture shows the first 0.001 inch of surface to contain less nitrogen than sample N3 nitrided for the same time at 950 degrees Fahr. in an aged bath. The second and third 0.001 inch show a nitrogen content equivalent to that of the steel itself. A steeper nitrogen gradient is indicated for the sample nitrided in a new bath as compared with samples nitrided in an aged bath.

Table IV

Nitrogen Determinations of Nitrided Samples. Various Temperatures—Constant Time Series. Aged Bath Used with Nickel Alloy Pots. Bath Was Nickel Contaminated

Sample No.	Preheat 30 Minutes at Temp. Degrees Fahr.	Nitride	(CN) of Bath Per Cent	Subsequent Maximum Removal of Runout of Surface by Sample Grinding O. K. = < 0.0002"	Nitrogen Determinations Depth of Cut 0.000" to 0.001"	0.0005" to 0.0015"	0.001" to 0.002"	0.0015" to 0.0025"	0.002" to 0.003"	0.0025" to 0.0035"	0.003" to 0.0045"
N1	850	850		None	0.90%	.....	0.05%	.....	0.03%	.....	.....
N2	850	850	23.7	0.0005"	.....	0.04%	.....	0.02%	.....	0.02%	.....
N3	950	950	23.6	None	0.22%	.....	0.03%	.....	0.02%	.....	.....
N4	1050	1000	20.47	None	0.32%	.....	0.001 to 0.00225" 0.02%			0.00225 to 0.00325" 0.02%	
N25	1050	1050	20.8	None	O. K.	0.000" to 0.0023" 0.104%					
N5	1150	1150	20.3	None	O. K.	0.34%	.....	0.02%	.....	0.02%	.....
N6*	1250	1250		0.0005"	O. K.	.....	0.18%	.....	0.07%	.....	0.02%
N7	1250	1250	20.19	None	O. K.	0.000 to 0.002" 0.24%		0.002 to 0.003" 0.01%		0.003 to 0.0045" 0.005%	
N17	None	None	....	.....	.....	0.000 to 0.002" 0.006%					

*Bar No. 6 did not true out to a clean surface on removal of 0.0005 inch of surface by grinding.

Table V

Nitrogen Determinations of Nitrided Samples, Various Times—Constant Temperature (1050 Degrees Fahr.) Series. Aged Bath Used Except for Specimens Nos. 13 and 14. Nickel Alloy Pot Used and Bath Was Nickel Contaminated

Sample No.	Preheat 30 Minutes at Temperature	Nitriding Time at 1050° F.	Per Cent (CN) of Bath	Per Cent Nitrogen in Various Depths of Cuts												
				0.000 to 0.001"	0.000 to 0.00125"	0.0005 to 0.0015"	0.000 to 0.002"	0.000 to 0.0023"	0.000 to 0.003"	0.001 to 0.00225"	0.00125 to 0.00225"	0.0015 to 0.0025"	0.002 to 0.003"	0.00225 to 0.00325"	0.0025 to 0.00325"	0.0025 to 0.0035"	0.001 to 0.00475"	0.003 to 0.004"	0.00475 to 0.00575"	0.000 to 0.001"†
P 1	1025° F.	3 min.	21.4	.....	.....	.....	.....	.....	0.030	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.06
P 2	1025° F.	10 min.	21.4	.....	.....	.....	.....	.....	0.041	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.093
P 3	1025° F.	30 min.	21.4	.....	.....	.....	.....	.....	0.059	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.15
N25	1050° F.	30 min.	20.8	.....	.....	.....	.....	0.104	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.21
P 4	1025° F.	90 min.	21.4	.....	.....	.....	.....	.....	0.095	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.26
N16	1050° F.	90 min.	20.19	.....	0.36	.....	.....	.....	.....	.....	0.02	.....	.....	0.01	.....	.....	.....	.....	.....	0.43
N 8	1050° F.	3 hrs.	.....	.....	.....	.....	0.39	.....	.....	.....	.....	.....	0.03	.....	.....	.....	0.01	.....	.....	0.58
N10	1050° F.	6 hrs.	19.8	1.09	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.22	.....	0.01	.....	1.09
N13	*1050° F.	30 min.	44.83	.....	.....	0.044	.....	.....	.....	.....	.....	0.007	.....	.....	0.006	.....	.....	.....	.....	.....
N14	1050° F.	30 min.	44.83	0.163	.....	.....	.....	.....	.....	0.006	.....	.....	.....	0.005	.....	.....	.....	.....	.....	0.163

*After nitriding 0.0005 inch removed from surface of bar by grinding.
†Nitrogen estimated 0.000 to 0.001 inch.

Table VI

Effect of Reheating Treatments on the Nitrogen Content. Constant Preheating and Nitriding Times and Temperatures. An Aged Bath Was Used with Nickel Alloy Pot. The Bath Was Nickel Contaminated

Sample No.	Reheating Treatments After Nitriding	Runout of Bars O. K. = Under 0.0002"	Nitrogen Determinations 0.000–0.001"	0.001–0.002" 0.001–0.0022"	0.002–0.003" 0.0022–0.0032"	Nitrogen Calculated to 0.000–0.001"
N 4	None	O. K.	0.32%	0.02%	0.02%	0.32%
N11	1100° F. 1 hour	0.00025"	0.20%	0.04%	0.002–0.0035" 0.01%	0.20%
N12	1300° F. 2 hours	O. K.	0.000–0.0012" 0.029%	0.0012–0.0022" 0.02%	0.0022–0.0032" 0.01%	0.030%
N15	1300° F. 2 hours	O. K.	0.032%	0.02%	0.01%	0.032%

All samples were approximately 1.7 inches diameter x 5½ inches long. Sample N12 was in annealed condition at time of nitriding.

The last column of Table V is an estimation of the nitrogen in the first 0.001 inch of surface of the various samples. Some liberty was taken in making these estimations but a consideration of all data would indicate them to be reasonably accurate.

Table VI shows the effect on the nitrogen content of nitrided high speed steel which was reheated after nitriding. Sample N15 prior to nitriding was treated as follows: Preheat 1550 degrees Fahr. for 35 minutes; high heat 2350 degrees Fahr. for 8.5 minutes; quenched in oil and tempered at 1080 degrees Fahr. for 1.5 hours after which it had a hardness of Rockwell C 63. The sample was then ground true and an additional 0.005 inch removed from the surface before nitriding.

The samples were placed in a vertical position in a perforated basket and were preheated at 1050 degrees Fahr. for 30 minutes at temperature. The basket containing the samples was transferred to the nitriding bath for a 30-minute immersion at 1000 degrees Fahr. The bath analyzed 20.47 per cent cyanogen. After nitriding, cooling and cleaning, samples N12 and N15 were pack annealed in cast iron chips at 1300 degrees Fahr. for 2 hours at temperature. The pipe containing the samples was cooled in silocel. Sample N15 showed a Rockwell C of 44 after the 1300-degree Fahr. anneal.

Examination of Table VI indicates that one-third of the nitrogen was lost on reheating sample N11 to 1100 degrees Fahr. for 1 hour. The analytical comparison between samples N12 and N15, or between a hardened and nitrided and an annealed and nitrided

Table VII

Nitrogen Determinations of Five Samples Nitrided at the Same Time at 1050 Degrees Fahr. for 30 Minutes for Estimation of Nitrogen Gradient Using an Aged Bath and Nickel Alloy Pot

Sample No.	Diameter of Bars Before Nitride	Diameter of Bars After Nitride	Amount Removed from Surface	Cuts for Analytical Samples Relative to Surface	Per Cent Nitrogen
N25	1.7150"	1.7149"	None	0.000 to 0.0023"	0.104
N21	1.7149"	1.7149"	0.0001" polished off surface	0.0001 to 0.0021"	0.063
N22	1.7148"	1.7149"	0.0002" ground off surface	0.0002 to 0.0022"	0.067
N23	1.7149"	1.7148"	0.0003" ground off surface	0.0003 to 0.0023"	0.056
N24	1.7150"	1.7148"	0.0004" ground off surface	0.0004 to 0.0029"	0.043

sample, was to gain substantive proof that the assumption, that an annealed surface would absorb nitrogen to the same extent as a hardened surface, was reasonably correct. It was felt that a temperature of 1300 degrees Fahr. would make the treated sample soft enough to be machined with a carbide tool although it was not anticipated that this treatment would reduce the nitrogen content to such a small amount. The nitrogen analyses of the first 0.001 inch of surface indicate that only one-tenth of the nitrogen was retained. The nitrogen in the first 0.001 inch of the annealed and nitrided and treated and nitrided samples are practically identical. While this does not definitely indicate that a hardened surface will absorb nitrogen at the same rate as an annealed surface it is at least some indication that this may be true.

Table VII gives the results of nitrogen determinations made on five annealed bars which were preheated at 1050 degrees Fahr. for 30 minutes at temperature and then nitrided at 1050 degrees Fahr.

Table VIII

Carbon Analysis of Surface Cuts of Nitrided Samples Using An Aged Bath and Nickel Alloy Pots

Sample No.	Nitriding Degrees Fahr.	Nitriding Time Minutes	Surface Removed by Grinding	Carbon Analyses Depth of Cuts 0.000" to 0.001"	0.0005" to 0.0015"	0.001" to 0.002"	0.0015" to 0.0025"	0.000" to 0.002"
N 1	850	30	None	0.85%	.....	0.69%	.....	.....
N 2	850	30	0.0005"	.....	0.70%	.....	0.704%	.....
N 3	950	30	None	0.99%	.....	0.69%	.....	.....
N 5	1150	30	None	0.94%	.....	0.69%	.....	.....
N 6	1250	30	0.0005"	.....	0.68%	.....	0.72%	.....
N 7	1250	30	None	.....	.....	.....	.....	0.88%
N 8	1050	180	None	.....	.....	.....	.....	0.87%
N10	1050	360	None	1.63%	.....	.....	.....	.....
N14	1050	30	None	1.18%	.....	.....	.....	.....

for 30 minutes. After rough grinding, the bars were given a stress relieval treatment at 1100 degrees Fahr. and then ground to a good tool room finish. The samples were preheated in a vertical position in a perforated basket and the basket transferred to the nitriding bath. After nitriding the bars were checked for distortion and found to be under 0.0001 inch for "runout". After nitriding, various small amounts of surface thickness were removed and cuts of about 0.002-inch depth of the new surfaces obtained. The results of the nitrogen determinations given in Table VII show the nitrogen gradient from the surface to 0.004 inch below surface is quite evenly decreasing.

A mathematical consideration of the probable nitrogen content of the first 0.0001 inch of surface is given in the appendix. The nitrogen analysis data given in Table VII were used for these calculations, but the data are insufficient to draw reliable quantitative conclusions. However, under the nitriding conditions imposed there is indicated a nitrogen content of approximately 0.8 per cent in the first 0.0001 inch of surface.

The black color of the nitrided surfaces and the sooty chips obtained in machining some of the specimens suggested the presence of considerable surface carbon. Consequently, small portions (0.2 gram of the cuts 0.000 to 0.001 inch and 0.5 gram of the cuts 0.000 to 0.002 inch) of the nitrogen analytical samples were taken for carbon analysis. Numbers N1, N2, N3, N5, N6 and N7 of Table IV and numbers N8, N10 and N14 of Table V were analyzed for carbon with the results tabulated in Table VIII.

Due to the small weight of the analytical samples used for the carbon determinations listed in Table VIII no high degree of accuracy is to be expected. The carbon analyses are probably accurate to within plus or minus 0.04 per cent. The analyses show very conclusively that there is a considerable amount of carbon adhering to the nitrided surfaces as it does not appear likely to have been absorbed by the steel. In order to form some estimate of the disposition of this carbon a number of additional samples were prepared for carbon analysis.

A number of the bars used for the nitrogen determinations were reground so as to remove an additional 0.010 inch from the surface. These bars were then nitrided for various periods at various temperatures. After nitriding, the bars were spotted with an abrasive eraser and micrometered for size and then carefully sand blasted.

Table IX

Carbon Analyses of Surface Cuts of Nitrided Samples. Aged Bath with Nickel Alloy Pots

Sample No.	Diameter of Samples Before Nitride	Diameter of Samples After Nitride	Diameter of Samples After Sand-blast	Preheating 30 Min. at Temperature Degrees Fahr.	Nitrided	(CN) of Bath	Black Residue Not Soluble in Water†	Carbon 0.000" to 0.002"	Carbon 0.002" to 0.004"
1A	1.7360"	1.7360"	1.7360"	850	850° F. 30 Min.	19.8%	0.3062 gms.	0.71	0.705
2A	1.7360"	1.7360"	1.7360"	950	950° F. 30 Min.	19.8%	0.1972 gms.	0.71	0.704
3A	1.7375"	1.7375"	1.7373"	1050	1050° F. 30 Min.	19.8%	0.2589 gms.	0.745	0.71
4A	1.7340"	1.7338"	1.7338"	1050	1050° F. 90 Min.	.....	0.4426 gms.	0.735	0.71
5A	1.7380"	1.7378"	1.7377"	1050	1050° F. 180 Min.	19.2%	0.5963 gms.	0.74	0.71
6A	1.7370"	1.7370"	1.7369"	1100	1100° F. 30 Min.	18.5%	0.1830 gms.	0.73	0.70
13A	1.7370"	.....	1.7370"	1050	*1050° F. 30 Min.	44.5%	0.2350 gms.	0.73	0.71
14A	1.7370"	.....	1.7370"	1050	*1050° F. 90 Min.	44.5%	0.2751 gms.	0.75	0.71

*Samples 13A and 14A were nitrided in a freshly prepared 60-40 mixture. Nitriding temperature plus or minus 10 degrees Fahr.

†This black residue was obtained by placing the samples in a large beaker of distilled water after they had cooled to room temperature from the nitriding bath. The loosely adherent brownish-black deposit was brushed from the surface, filtered into weighed Gooch crucibles, washed free from cyanide, dried and then weighed.

The sand blasting was very light in an endeavor to remove the dark color only. The bars were again micrometered for size in the same three relative locations used on the prior measurements. Table IX is a tabulation of the results of the carbon analyses on two successive cuts of 0.002 inch on each bar.

The results of the carbon determinations given in Tables VIII and IX indicate that considerable carbon adheres to the nitrided surfaces. There is little difference, as shown in Table IX, in the carbon content of the first 0.002 inch of samples nitrided at 1050 degrees Fahr., 30 minutes, 1050 degrees Fahr., 90 minutes and at 1100 degrees Fahr., 30 minutes. This would indicate little or no cementation takes place. That the carbon should be somewhat higher on the first 0.002 inch of the surface is probably due to the fact that in nitriding there is a microscopic pitting of the surface. These pits appear to contain small carbon particles which are not dislodged by the light "dusting off" under the sand blast. Another contributing cause of the higher carbon may be the trapping of carbon particles by the nickel which plates onto the surfaces of high speed steel nitrided in a bath contaminated with nickel.

Samples of high speed steel which are nitrided show on cooling

to room temperature a more or less reddish-brown color suggestive of iron oxide. Several additional samples similar to those of Table IX were nitrided at 1050 degrees Fahr. for 30 minutes. Two samples were preheated at 1050 degrees Fahr. prior to nitriding and two not preheated. The brownish-black residue adhering to the nitrided surface was freed of cyanide by filtering on filter paper and washing with hot water. After drying the samples were analyzed with the results given below:

Samples not preheated

C	Fe	Ni	Cr
1.16	62.6	0.35	3.71

The preheated samples analyzed for iron content only showed this to be 63.1 per cent.

From the above it will be seen that considerable carbon forms on the steel surfaces probably due to the decomposition of CO which in turn results from the decomposition of the cyanates. The high percentage of iron and chromium may be derived from the erosion of the high speed steel by the salt. It may be possible that some of the iron contained in solution in the molten salt may plate onto the immersed surfaces. On removal from the bath and on cooling to room temperature this iron may oxidize to iron oxide. The nickel is derived from the nickel in solution in the bath.

When it was learned that the nickel contamination of the bath was affecting the results it was thought desirable to recheck the nitrogen content of consecutive 0.001-inch cuts on samples nitrided in an aged bath free from nickel. It was decided to explore, in steps of 50 degrees Fahr., the apparent useful nitriding temperature range, viz.: 900 to 1100 degrees Fahr. Two annealed bars were prepared for nitriding at each temperature by accurately grinding between centers. The bars were placed in a vertical position in a perforated basket and preheated to the same temperature as that used for nitriding. After holding at the preheating temperature for 20 minutes the baskets were transferred to the nitriding bath and moved up and down several times after immersion. No subsequent agitation was given the immersed samples. The bath was sampled for analysis 15 minutes after immersion. Concurrently there were nitrided at each temperature a micro-polished annealed sample (No. 95 to No. 99 inclusive) and two micro-polished treated samples (No. 80 to No. 89 inclusive) of high speed steel. The micro-polished samples were not preheated prior to immersion.

Table X

Nitrogen Analysis of Surface Cuts on Bars Nitrided in a Bath Free from Nickel Contamination. Variable Temperature—Constant Time Series

No.	Diameter of Bars: Before Nitriding	Diameter of Bars: After Nitriding	"Run Out" of Bars	Preheat 20 Min. at Temp. Degrees Fahr.	Nitriding 30 Min. at Temp. Degrees Fahr.	Analysis of Bath: Per Cent CN	Analysis of Bath: Per Cent CNO	Brownish Black Residue Not Water Soluble (Grams)	Subsequent Removal of Surface by Grinding	Nitrogen Per Cent: 0.000" to 0.002"	Nitrogen Per Cent: 0.0005" to 0.002"	Nitrogen Per Cent: 0.000"† to 0.0005"
C 3	1.6900"	1.6899"	0.0000"	900	900	25.55	15.04	0.1053	0.0005"	.....	0.013	0.025
C 4	1.7231"	1.7230"	0.0000"						None	0.016	.....	
C 5	1.6900"	1.6900"	0.0000"	950	950	25.17	14.73	0.2073	0.0005"	.....	0.015	0.087
C 6	1.7080"	1.7080"	0.0000"						None	0.033	.....	
C 7	1.6890"	1.6890"	0.0001" one end 0.0000"	1000	1000	24.44	14.48	0.2788	0.0005"	.....	0.027	0.208
C11	1.7230"	1.7230"	0.0000"	1050	1050	23.83	14.26	0.3180	None	0.079	.....	0.317
C12	1.7221"	1.7219"	0.0000"						0.0005"	.....	0.027	
C13	1.7080"	1.7080"	0.0000"						None	*0.085	.....	
C14	1.7079"	1.7079"	0.00005" one end 0.0000"						0.0005"	.....	0.025	
C16	1.6539"	1.6539"	0.0000"	1100	1100	23.63	14.28	0.3581	None	0.105	.....	0.345

*Cut 0.000 to 0.0024 Inch.
†By difference.

Table XI

Recheck of Nitrogen Gradient in Samples Nitrided in a Freshly Prepared Mixture of 60% NaCN and 40% KCN. Pressed Steel Pot. Very Slight Nickel Contamination from Thermocouple Protection Tube

No.	Preheat 20 Min. at Temp. Degrees Fahr.	Nitrided Degrees Fahr.	CN	CNO	CO_3	Nitrogen Determinations 0.0000" to 0.001"	0.001" to 0.002"	0.002" to 0.003"
N170	1050	1050 ± 10 30 min.	Start 45.22%	1.14%	1.87%	0.174	0.009	0.009
N200	1050	1050 ± 10 90 min.	44.70% Finish	.....	.....	0.197	0.124	0.013

After nitriding and removing the adherent salt and surface deposit one of the companion bars of each temperature was ground to remove 0.0005 inch from the surface.

The histories of the various samples are given in Table X. Chips were obtained from the bars for nitrogen analyses using tantalum carbide tools. On the "as-nitrided" bars, cuts of 0.000 to 0.002 inch were made and on the bars from which 0.0005 inch was ground after nitriding, cuts of 0.005 to 0.002 inch were made. The prior experiments had indicated the bulk of the nitrogen to be within the first 0.0005 inch of surface at the temperatures of 900 to 1100 degrees Fahr. for 30-minute periods of immersion. The analyses under the conditions imposed permitted the evaluation of the nitrogen percentage in the first 0.0005 inch of surface.

Table XI is a tabulation of the nitrogen determinations on three successive cuts of 0.001 inch made on two samples nitrided respectively 30 and 90 minutes at 1050 degrees Fahr. in a freshly prepared 60-40 mixture. These samples were immersed at the same time. Sample N170 was run to check the analyses of three successive cuts on sample N14, Table V. Sample N14 had been nitrided previously in another freshly prepared bath. Sample N170 nitrided for 30 minutes showed on the cut 0.000 to 0.001 inch a nitrogen content of 0.174 per cent. On the cut 0.001 to 0.002 inch the nitrogen content is comparable to that found in the steel itself. This duplicates the result of the first test as regards a steep nitrogen gradient. The sample nitrided for 90 minutes in the same bath shows only slightly more nitrogen (0.197 per cent) in the first 0.001 inch as compared to (0.174 per cent) the first 0.001 inch of sample nitrided for 30 minutes. On sample N200 nitrided for 90 minutes the second and third 0.001 inch show an increase or diffusion of

Table XII

The Determination of the Percentage of Nitrogen by Difference on the First 0.0005 Inch of Surface. Bars Electrically Insulated During Nitriding. The Bath Was Free from Nickel Contamination

No.	Preheat 20 Min. at Temp. Degrees Fahr.	Nitriding 30 Min. at Temp. Degrees Fahr.	Per Cent CN of Bath	Brownish Residue on Samples Not Water Soluble (Grams)	Subsequent Removal of Surface by Grinding	Nitrogen Determinations 0.000 to 0.002"	Nitrogen Determinations 0.0005 to 0.002"	Nitrogen Determinations 0.000 to 0.0005" by Difference
N 33					0.0005"	.....	0.017	
N 44	900	900	24.8	0.1228	None	0.036	.....	0.093%
N 55					0.0005"	.....	0.018	
N 66	950	950	23.8	0.3449	None	*0.050	.....	0.166%
N 77					0.0005"	.....	†0.022	
N111	1000	1000	23.6	0.4151	None	‡0.082	.....	0.280%
N122					0.0005"	.....	0.035	
N133	1050	1050	24.1	0.7064	None	0.092	.....	0.263%

*Cut 0.000 to 0.0022"
†Cut 0.0005 to 0.0022"
‡Cut 0.000 to 0.00215"

nitrogen. It would appear that if tools nitrided in a freshly prepared bath were to be given a long immersion period there should be no excessive brittleness as shown by short time immersion periods. The comparatively low nitrogen content of the first 0.001 inch of the sample nitrided for 90 minutes as compared to the sample 30 minutes and the indication of nitrogen diffusion would suggest a lower surface nitrogen content on the 90-minute sample. This appears to be the case as supported by the micro-hardness indentation numbers obtained by testing a hardened and micro-polished sample nitrided for 90 minutes in a freshly prepared bath.

Table XII gives the results of nitrogen determinations on bars nitrided at 900 to 1050 degrees Fahr. in increments of 50 degrees Fahr. Two bars were nitrided at each temperature, then one bar of each pair was ground to remove 0.0005-inch depth from surface. The results of the nitrogen determination as calculated to the first 0.0005 inch of surface on the noninsulated samples of Table X and the insulated samples of Table XII show considerable disparity at the 900 and 950-degree Fahr. temperatures. This may be due to several factors, one of which might be the interference of the surface deposit and another, the variable circulation of the bath. The noninsulated samples were placed in a vertical position in perforated baskets, while the insulated samples were suspended in a vertical position from glass rods by means of a $\frac{1}{32}$-inch diameter soft iron wire. The bath containing the insulated sample probably

Table XIII

Weight Change of Rectangular Samples (0.307x0.98x2.1 Inches) Nitrided in a Bath Free from Nickel Contamination. Comparison of Samples Preheated and Samples Not Preheated Prior to Nitriding

No.	Preheat Degrees Fahr.	Nitriding Degrees Fahr.	Analysis of Bath: Per Cent CN	Analysis of Bath: Per Cent CNO	Weight (Grams) Before Nitriding	Weight (Grams) After Nitriding	Net Change (Grams)	Weight After Scrubbing (Grams)	Gross Change in Weight (Grams)
301	900—20 min.	900—30 min.	25.55	15.04	94.2645	94.2544	—0.0101	94.2519	—0.0126
391	None	900—32 min.			94.4139	94.4083	—0.0056	94.4068	—0.0071
401	950—20 min.	950—30 min.	25.17	14.73	94.5452	94.4810	—0.0642	94.4695	—0.0757
311	None	950—32 min.			94.2165	94.1847	—0.0318	94.1783	—0.0382
321	1000—20 min.	1000—30 min.	24.44	14.48	94.1485	94.1033	—0.0452	94.0942	—0.0543
331	None	1000—32 min.			94.2104	94.1819	—0.0285	94.1779	—0.0325
341	1050—20 min.	1050—30 min.	23.83	14.26	94.0727	94.0418	—0.0309	94.0324	—0.0403
371	None	1050—32 min.			94.2279	94.2092	—0.0187	94.2074	—0.0205
361	1100—20 min.	1100—30 min.	23.63	14.28	94.1026	94.0829	—0.0197	94.0795	—0.0231
381	None	1100—32 min.			94.1072	94.1069	—0.0003	94.1039	—0.0033
*351	None	1100—32 min.	23.16	14.74	94.1306	94.1356	+0.0050	94.1335	+0.0029
411	None	1100—32 min.			94.6470	94.6258	—0.0212	94.6252	—0.0218

*Sample No. 351 electrically insulated.

circulated more freely while the perforated basket acted more or less as a baffle to convection.

The insulated samples received more manual agitation after immersion due to the adjustment in spacing the bars as suspended from the glass rods. It may be possible that the low nitrogen results obtained on samples No. C3 and No. C5 may have been due to chemical nonequilibrium in the bath due to nitriding immediately after cooling down from a higher temperature.

Immediately following the nitriding of each pair of analytical samples there were nitrided a pair of treated and ground high speed steel samples approximately 0.307 x 2.17 x 0.98 inches, one of which was preheated and the other not preheated. These samples were carefully prepared and weighed. After nitriding, the samples were reweighed, both before and after scrubbing with emery powder and oil to remove surface smudge. The results of this test are given in Table XIII. The preheated samples show a greater loss in weight than companion samples not preheated probably due to the erosion by the bath of the thin layer of oxide formed in preheating. There is a greater loss in those samples nitrided at 950 degrees Fahr. as compared to those nitrided at 900 degrees Fahr. There is a diminishing loss in weight from 950 to 1100 degrees Fahr. which may be explained by the increased amount of nitrogen absorbed with increase in temperature. The small change in weight of sample No. 381 led us to nitride a duplicate sample at 1100 degrees Fahr. One sample

was immersed without preheating as before and another sample, also not preheated, was electrically insulated. It was found that the electrically insulated sample increased in weight while the non-insulated sample had decreased in weight. It was this discrepancy that caused the investigation of the galvanic action of the bath which was described earlier in the paper.

7. The Hardness of the Nitrided Surfaces. It has long been recognized that the hardness at the surface of hardened and tempered high speed steel is greatly increased by the nitriding process; it has not been generally recognized that the surface hardness of annealed high speed steel is increased to about the same hardness as the surface of hardened and tempered high speed steel when the annealed high speed steel is subjected to the nitriding treatment. This can be explained by the fact that the depth of the hardened case resulting from a short immersion period is so extremely shallow that when it is tested by a file the surface is broken even with a very light pressure.

Observations from tools in use have indicated that the nitrided cases of hardened and tempered high speed steel apparently vary greatly in brittleness. About the only test possible to gage this brittleness has been to nitride a sharp-edged hardened high speed steel tool for from 10 to 20 minutes and scratch a pane of common window glass with it. A brittle edge will have dulled noticeably after scratching an inch or two, while a properly nitrided edge should scratch 10 or 15 inches without appreciable dulling; under the best conditions even as much as 60 inches of window glass may be scratched by such a tool before becoming excessively dulled.

While the nitrided surface of a high speed steel tool is extremely hard, none of the present-day hardness testing methods permit of a quantitative evaluation of this superhardened surface. The Brinell, Rockwell and Firth-Vickers tests give little or no indication of increased hardness. The Superficial Rockwell, the Monotron and the Firth-Vickers using light loads give a quite consistent indication of an increased hardness. However, the order of difference, that of several points, is too small to be of much consequence.

In practically all of the literature on hardness the distinction between surface and internal hardness is the distinction between the location of the test areas (or impressions) in respect to the specimen as a whole. The word "surface" as used in hardness testing is given a broad terminology even as we have given it in this inves-

tigation. The word "surface" as frequently used covers considerable territory beyond that of area.

One may harden a 1.00 per cent carbon tool steel and measure the hardness of one of its surfaces by means of the Rockwell or other hardness testing instruments. The tool or specimen may be ground all over and again one may measure the hardness of the new "surface". One may section the tool with a rubber nicking wheel, thereby creating new surfaces. When the hardness of the sectioned surfaces is determined the values are usually designated as the internal hardness.

The usual methods of measuring hardness do not evaluate the surface hardness of any surface, in fact a relative evaluation of the hardness number of a surface may never be made unless some future genius may devise a ray of light reflection method. Since the definition of surface is that which has area but no depth, then no method which requires depth could permit of an evaluation of the relative surface hardness. All the present-day methods of hardness testing require a relatively thick specimen. The depth of the impression or the influence of the depth on an impression is so great that only an average hardness number of a considerable three dimensional or hemispherical space is obtained.

Concurrently with the analytical samples listed in Tables IV, V and VI, there were nitrided a number of treated high speed steel samples for hardness and microscopic examination. The test samples were made from bars $\frac{7}{16}$ x $1\frac{1}{16}$ inch cut to $1\frac{1}{8}$-inch lengths. The steel had the following composition:

C	Mn	P	S	Si	Cr	Ni	V	W
0.685	0.21	0.021	tr.	0.33	3.99	0.078	0.97	17.84

In all the "surface" hardness tests and the microscopic examinations to follow, the test samples were from bars of this same size and were from this heat of steel.

The test samples were prepared by milling off 0.045 inch from the two broad sides, and 0.015 inch from the two thin sides. The samples were treated as follows:

1550 degrees Fahr.—12 minutes
2350 degrees Fahr.— 2 minutes 15 seconds—Quench in oil
1080 degrees Fahr.—$1\frac{3}{4}$ hours
Rockwell C—63.5-63.75

After tempering, the samples were trued on the two broad sides by grinding and an additional 0.003 inch removed. The thin sides

Table XIV

Approximate Depth of Nitrided Case As Indicated by Microscopic Examination Both Aged and Fresh Bath Used, with a Nickel Alloy Pot

Sample No.	Preheat 30 Min. at Temp.	Continued Heating Minutes	Nitriding Minutes	Per Cent (CN) of Bath	Rockwell Hardness A Scale	Rockwell Hardness C Scale	Approximate Microscopic Depth of Nitrided Case—Etchant 4% Nital
1	850° F.—30	....	850° F.— 30	23.7	83.25	63.75	None
2	850° F.—30	850° F.—30	None	....	83.2	63.75	.....
3	950° F.	..... .	950° F.— 30	23.6	83.25	63.75	0.0005"
4	950° F.	950° F.— 30	None	....	83.25	63.75	.....
*20	1050° F.	.....	1000° F.— 30	20.47	83.2	63.5	0.0010"
21	1050° F.	.....	1000° F.— 30	20.47	83.2	63.7	0.0015"
19	1000° F.—30	....	1000° F.— 30	21.6	83.25	63.5	0.0015"
10	1000° F.—30	1000° F.— 30	None	....	83.0	63.5	.....
5	1150° F.—30	.....	1150° F.— 30	20.3	82.25	62.0	0.0025"
6	1150° F.—30	1150° F.— 30	None	....	82.25	62.0	.....
*11	1250° F.	.....	1250° F.— 30	20.2	78.5	55.0	0.0035"
12	1250° F.	1250° F.— 30	None	....	78.5	55.0	.....
22	1050° F.	.....	1050° F.—180	20.2	83.9	64.2	0.0032"
*14	1050° F.	1050° F.—180	None	....	83.2	63.25	.....
23	1050° F.	.....	1050° F.—360	19.8	84.0	64.3	0.004"
*25	1050° F.	1050° F.—360	None	....	83.0	63.4	.....
15	1050° F.	.....	1050° F.— 30	44.8	83.0	63.5	0.001"
17	1050° F.	.....	1050° F.— 30	44.8	83.0	63.5	.....
*18	1050° F.	..... .	1050° F.— 90	44.8	83.0	63.5	0.002"
*16	1050° F.	..... .	1050° F.— 90	44.8	83.0	63.75	.....
*8	1050° F.	.....	1050° F.— 90	20.2	83.25	63.5	0.002"
*13	1050° F.	1050° F.— 90	None	....	83.25	63.75	.....
7	None	.....	(see note†)	....	83.0	62.5	0.004"
24	None	.....	(see note†)	....	83.0	62.5	.....

*Top surfaces of these samples were not lapped prior to preheating or nitriding treatments, "as ground" surfaces nitrided.

†Curiosity nitrided samples. These samples were placed in the nitriding bath at 7:00 P. M. at about 1175 degrees Fahr. and left in the bath over night. The bath was kept molten by means of a small current input, using a transformer. Temperature dropped to 825 degrees Fahr. by 8:00 A. M. the following morning. Bath was still molten with a top crust about ½" thick but with a hole in the crust of about 1" diameter. The current was turned on using the regular control. Bath reached 1050 degrees Fahr. at 9:00 A. M. The samples were left in the bath until 11:20 A. M. at this temperature.

Samples No. 15, 16, 17 and 18 were nitrided in a freshly prepared mixture of 60% NaCN and 40% KCN.

and ends were ground to a clean surface only. After grinding a number of samples were lapped on one of the broad surfaces. As treated, as lapped, and as nitrided one surface is denoted as the top side, which side was face upward on the trays in the nitriding basket.

After all treatments the samples were nicked in half by means of a rubber nicking wheel. The lapped nitrided surfaces were then repolished to a sufficient degree to permit of micro hardness tests on the surface. One-half of each specimen was prepared for microscopic examination of the cross section of the nitrided case by tightly clamping two samples together with a strip of 0.0015-inch thick copper sheet between, to preserve the edges against rounding.

Hardness of the Nitrided Cases: Examination of Table XIV reveals that the Rockwell A and C scale numbers are not increased

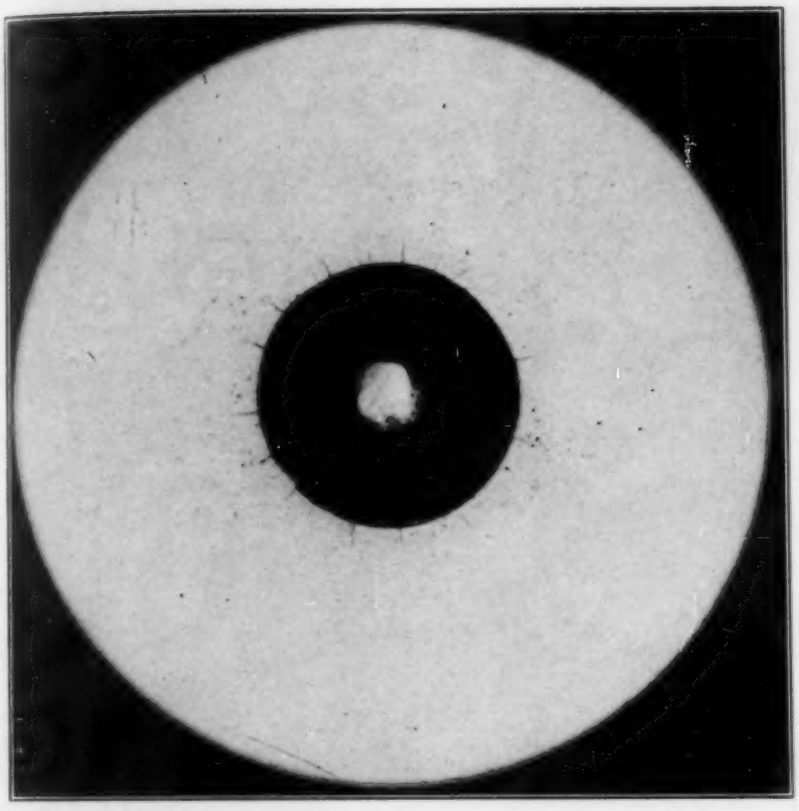


Fig. 4—Rockwell A Impression on Surface of Hardened and Drawn High Speed Steel. Nitrided at 1050 Degrees Fahr. 11 Minutes. Unetched. × 100.

by nitriding. Only samples No. 22 and No. 23 nitrided respectively 3 and 6 hours show any increase in hardness and that of the order of about one point for each scale. With the exception of samples No. 1 and No. 2 all the nitrided samples show radial cracks around the Rockwell A and C impressions. The radial cracks around the Rockwell impressions increase in magnitude as the time of immersion is increased. It is difficult to discern the cracks around impressions made on ground and nitrided surfaces due to their being masked by the surface etching or microscopic pitting.

If one micro-polishes the surface prior to nitriding, the cracks are easily discernible at a magnification of × 100 or less. Figs. 4 and 5 are micrographs at ×100 of Rockwell A impressions made on hardened high speed steel samples which were micro-polished and then nitrided respectively for 11 and 91 minutes at 1050 degrees Fahr. The radial cracks which increase in magnitude as the time of immersion is increased may readily be seen. The Rockwell testing of nitrided high speed steel surfaces is somewhat damaging to the

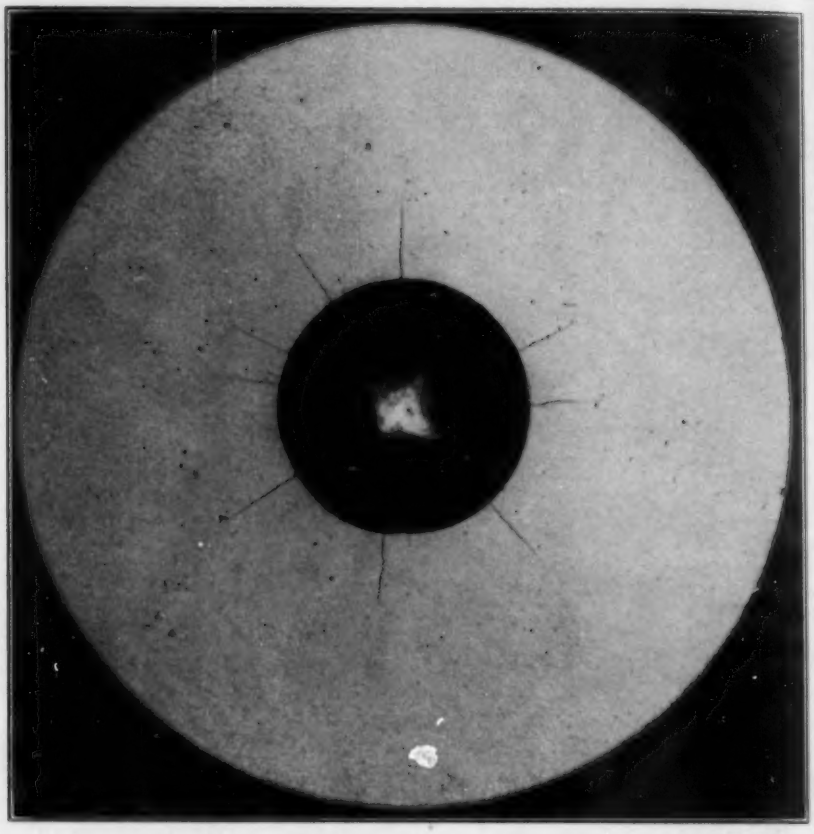


Fig. 5—Rockwell A Impression on Surface of Hardened and Drawn High Speed Steel. Nitrided at 1050 Degrees Fahr. 91 Minutes. Unetched. × 100.

diamond brales although not as hazardous as the use of brales in the testing of the nitrided cases of nitralloy steels. This is probably due to the hard "backing" of the hardened high speed steel.

Most of the samples listed in Table XIV were micro-polished after nitriding on those surfaces which had been lapped prior to nitriding. The micro-polished samples were tested for hardness by means of the Bierbaum Micro-character. The values obtained by this method were not deemed reliable indices of the hardness and have been omitted. Evidently the surface and subsurface carbides influenced the micro-cut to such an extent as to make the results useless.

A micro-indentation test recently developed at the National Bureau of Standards suggested possibilities for evaluating the surface hardness of nitrided high speed steel. This instrument was devised by Messrs. C. G. Peters and F. Knoop, respectively, Chief and Assistant of the Interferometry Section of the Bureau of Standards. The indenter, hereafter referred to as the Knoop indenter,

was designed by Mr. Knoop, patented by him and the patent assigned to the U. S. Government.

Fig. 6 is a sketch showing the detail of an impression made by the Knoop indenter. Fig. 7 is a sketch of the diamond indenter. A noteworthy characteristic of the type of indentation made by the Knoop indenter is the relatively large area of impression in relation to its depth. The major axis of an impression is about thirty times that of the depth.

The test instrument consists of a dash pot controlled beam on one end of which the indenter is carried. The beam and weights which are accurately calibrated permit of indenting a test specimen under loads of 2000, 1000, 500, 200, 100 and 50 grams.

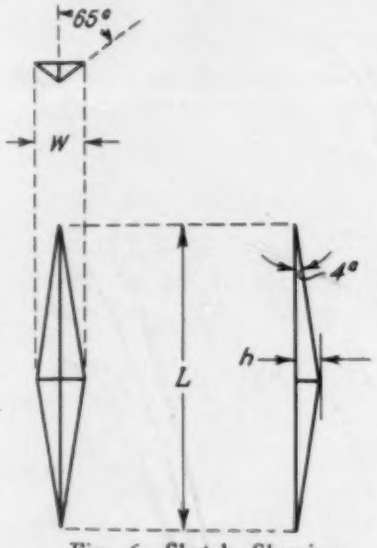


Fig. 6—Sketch Showing Detail of Impression Made by the Knoop Indenter.

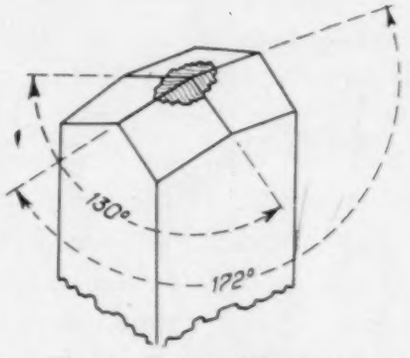


Fig. 7—Exaggerated Sketch of the Knoop Indenter Used in Making the Micro-Indentation Tests. Diamond Mounted in a Square Bar.

A sample to be tested is first prepared with a micro-polished surface. In making an impression the specimen is brought close to but not in contact with the indenter. A cam release permits the indenter to descend onto the specimen. The rate of descent is controlled by the dash pot which is adjusted for a 3 mm. descent in about 10 seconds. The contact of the indenter under the predetermined load is maintained for 20 seconds. The indenter is then raised by means of a lever attached to the cam. The indentation is magnified 100 to 500 times and the length of the major axis measured with a micrometer microscope. The hardness number which appears to be quite comparable to the Brinell number is computed by use of the following formulae:

Assuming the angles between the edges (Fig. 7) to be 130 and 172 degrees then the constant area and indentation number may be computed from the following expression:

$$\text{Constant} = \frac{\tan 4^\circ \times \tan 65^\circ}{2} = 0.07498$$

$$\text{Projected Area} = L^2 \frac{\tan 4^\circ \times \tan 65^\circ}{2}$$

in which L equals length in microns of the major axis of the impression or indentation mark.

$$\text{The Indentation Number} = \frac{\text{Load in Kg}}{\text{Projected Area in Sq. m/m}}$$

Figs. 8 and 9 are micrographs at ×200 which show the character of the indentations made by the Knoop indenter at 1000-gram loads.

The micro-hardness numbers included in this investigation were obtained by the Bureau of Standards in probing the possibilities of this test instrument for evaluating the hardness of the nitrided cases of nitrided high speed steel. The micro-indentation hardness results are published with the permission of the Bureau as a contribution to the evaluation of the comparative hardness of thin layers of the surface of nitrided high speed steel.

The micro-indentation hardness numbers tabulated in Table XV are not to be considered reliable surface hardness values. Due to the necessity of removing some of the surface in micro-polishing subsequent to nitriding more or less of the hard exterior was removed. However, a comparison of companion nitrided and non-

Table XV
Micro-Indentation Hardness Numbers of Samples of Hardened High Speed Steel Listed in Table XIV

Sample No.	Preheat 30 Min. at Temp. (Degrees Fahr.)	Continued Heating 30 Min. (Degrees Fahr.)	Nitriding 30 Min. (Degrees Fahr.)	Rockwell C	Micro-Indentation Hardness Number for Various Loads (Grams) 2000	1000	500	200	100
1	850	None	850	63.75	776	814	847	838	844
2	850	850	....	63.75	752	786	779	753	747
3	950	None	950	63.75	881	948	1004	1061	1104
4	950	950	....	63.75	...	810	822	...	...
21	1050	None	1000	63.7	944	1007	950	933	878
10	1000	1000	....	63.5	769	798	809	812	802
5	1150	None	1150	62.0	930	990	1021	1015	1023
6	1150	1150	....	62.0	...	744	747	...	...
11	1250	None	1250	55.0	817	872	873	924	920
12	1250	1250	....	55.0	598	603	612	592	606

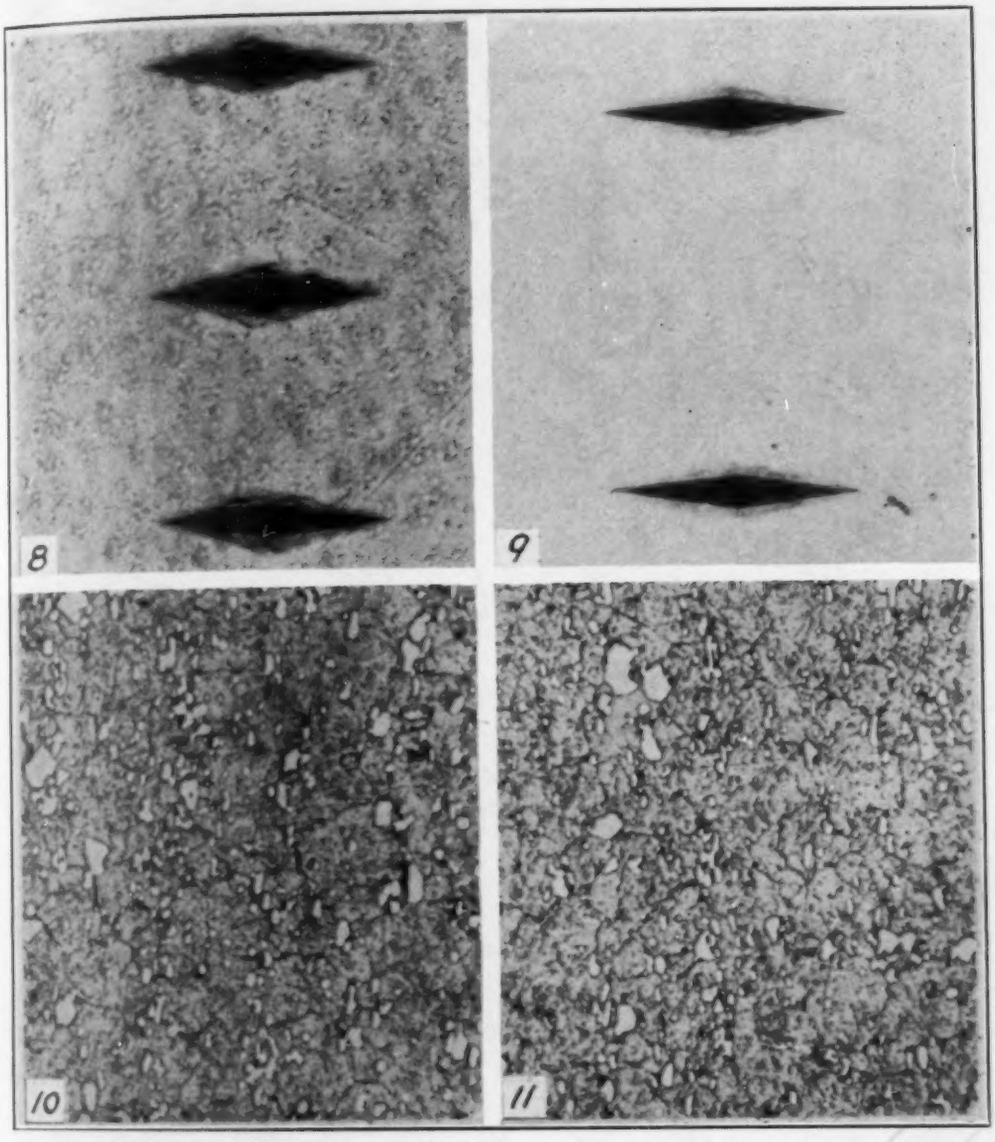


Fig. 8—Micrograph of Impression Made by the Knoop Indenter at 1000 Grams Load. Sample C of Table XVI. × 200.

Fig. 9—Micrograph of Impression Made by the Knoop Indenter at 1000 Grams Load. Sample E of Table XVI. × 200.

Fig. 10—Internal Microstructure of Sample C. Etching Time 1 Minute. Etchant 4 Per Cent Nital. × 500.

Fig. 11—Internal Microstructure of Sample E. Etching Time 1 Minute. Etchant 4 Per Cent Nital. × 500.

nitrided samples show a marked enhancement of the micro-indentation hardness number due to nitriding. On sample No. 3 a hardness number of 1104 at a 100-gram load is obtained compared to 810-822 for the companion sample not nitrided. Sample No. 21 was preheated at 1050 degrees Fahr. and in error nitrided at 1000 degrees Fahr. instead of 1050 degrees Fahr. The surfaces of this sample were in the "as ground" condition prior to nitriding necessitating

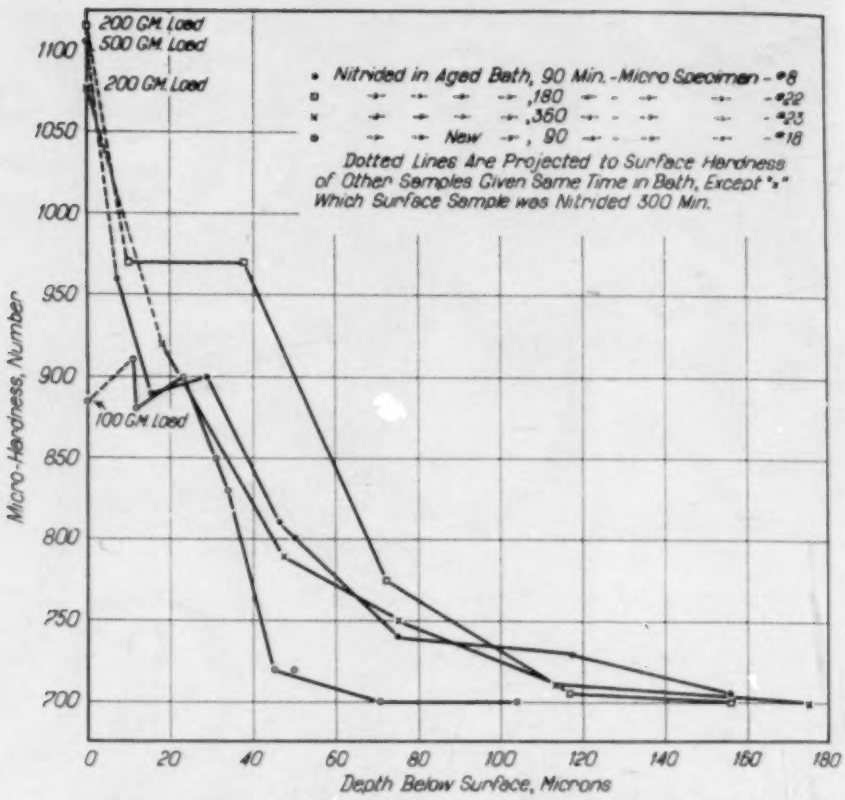


Fig. 12—Micro-Hardness Gradients of High Speed Steel Samples Nitrided at 1050 Degrees Fahr. for 31 Minutes. Unetched. × 100. Load 50 Grams.

the removal of a considerable amount of surface metal in micro-polishing for the micro-indentation test.

The surface of sample No. 11 nitrided at 1250 degrees Fahr. is considerably harder than the companion sample tempered only at 1250 degrees Fahr. The surface hardness is considerably reduced over that of samples nitrided at the lower temperatures due to the tempering of the high speed steel. The test results given in Table XV suggest a change in preparation technique if the hardness of the surface is to be more accurately gaged; i. e., micro-polishing of the test specimens prior to nitriding, which procedure was then followed.

In order to determine the micro-hardness gradient, samples No. 8, No. 22 and No. 23 nitrided respectively 90, 180 and 360 minutes at 1050 degrees Fahr. in an aged bath and No. 16 nitrided in a freshly prepared 60-40 mixture were sectioned with a nicking wheel. Two samples were clamped together tightly with a sheet of 0.0015-inch copper between and micro-polished.

The curves in Fig. 12 show the depth of impressions below the

Table XVI

Comparison of the Micro-Indentation Hardness of the Surface of High Speed Steel in the Following Condition: (1) Annealed; (2) Annealed and Nitrided; (3) Treated; (4) Treated and Nitrided in a Freshly Prepared Bath Mixture of 60 Per Cent NaCN-40 Per Cent KCN; and (5) Treated and Nitrided in an Aged Bath

Sample	Condition of Sample	Nitrided 1050 Degrees Fahr.	Per Cent (CN) of Bath	Repolishing After Nitriding	Rockwell C		Superficial 30 Kg. (227 Brinell)	Micro-Indentation Hardness for Various Loads (Grams)				
					As Hardened	As Nitrided		2000	1000	500	200	100	50
L	Annealed	None	.....	.....	18	....	....	223	235	230	...	...	...
M	Annealed	31 min.	23.0	Broadcloth	18	18	....	460	609	750	795	830	712
B	Treated	4 min.	Start				....						
			44.68	Broadcloth	64.5	64.5	....	843	892	925	992	1028	...
A	Treated	31 min.	44.54	Broadcloth	64.5	64.5	....	956	1025	1034	1078	1054	1043
			Finish	Canvas and Broadcloth	64.5	64.5	....	935	963	971	870	887	...
F	Treated	91 min.			64.5	....	....		889	889	...	...	...
C	Treated	None	.....	.....	64.5	....	....	751	755	744	...	...	...
E	Treated	None	.....	.....	64.5	....	81.0	827	871	886	926	860	...
H	Treated	4 min.	Start	Broadcloth	64.5	64.5	81.5	868	930	970	992	938	...
I	Treated	11 min.	23.0	Broadcloth	64.5	64.5	82.0	981	1033	1051	...	...	...
J	Treated	31 min.		Broadcloth	64.5	64.5	82.0	1057	1124	1110	...	...	...
G	Treated	91 min.		Canvas and Broadcloth	64.5	64.5	83.0						
			20.03	"O" Paper and Finer	64.5	64.2	83.5	1078	1085	1103	1077	1034	...
TEST BLOCK		.....			25.5				271				
TEST BLOCK		.....			47.1				472				
TEST BLOCK		.....			65-67				789				

Note: The microscopic case depths of samples B, A and F—showed 0.0005, 0.0010 and 0.0022 inch respectively.

surface plotted against the hardness number at 50-gram loads. The dotted lines are projected to the surface hardness numbers of other samples nitrided at the same temperature for the same or similar periods of time. Sample No. 16 nitrided in a new bath shows the steepest hardness gradient and a low surface hardness. Sample No. 23 nitrided for 360 minutes shows a steeper hardness gradient than sample No. 22 nitrided 180 minutes. This apparent discrepancy and the low hardness of the surface of sample No. 16 suggest the possibility of a reversible reaction as regards the absorbed nitrogen.

Table XVI is a tabulation of the comparative surface hardness results obtained in testing micro-polished high speed steel specimens in the following conditions: (1) annealed; (2) annealed and nitrided; (3) treated; (4) treated and nitrided in a freshly prepared 60-40 NaCN-KCN mixture; and (5) treated and nitrided in an aged bath. The micro-indentation hardness numbers of annealed sample "L" at indentation loads of 500 to 2000 grams is 223 to 235 which compares closely with the Brinell number of 227. The annealed and nitrided sample "M" (nitrided at 1050 degrees Fahr. for 31 minutes) shows a micro-indentation hardness number (at 100-gram load) of 830 as compared to 744, 755 and 751 (the hardness numbers at 500, 1000 and 2000-gram loads) for fully treated sample "E". As the indentation loads are increased in testing sample "M" the hardness numbers decrease due to the increased penetration of the indenter or the transmission of the load beneath the nitrided layer. The depth of penetration of the indenter for sample "M" is 8.3 microns (0.0003267 inch) for the 2000-gram load and 2.0 microns (0.000079 inch) for the 200-gram load.

Sample "B" which was nitrided for 4 minutes in a freshly prepared 60-40 bath shows a higher surface hardness number (1028) at a 100-gram load than sample "H" (860) treated for 4 minutes in an aged bath. Sample "A" nitrided for 31 minutes in the new bath shows a surface hardness comparable to sample "J" nitrided for the same time in an aged bath. There is a slight indication the hardness gradient of sample "J" is not as steep as sample "A". Sample "F" nitrided in a new bath for 91 minutes shows a relatively low surface hardness but a suggested depth of hardness at least comparable to sample "A".

Samples H, I, J and G nitrided respectively for 4, 11, 31 and 91 minutes in an aged bath at 1050 degrees Fahr. show a progressive increase in hardness (or nitrogen penetration) for all indenta-

tion loads. Sample "D" nitrided for 300 minutes shows a somewhat lower hardness at 500 and 1000-gram loads as compared to sample "G" under the same conditions. The depth of the indentation marks on sample "D" is 5.5 microns (0.0002185 inch) for the 2000-gram load and 1.5 microns (0.0000590 inch) for the 200-gram load.

Samples "C" and "E" present an anomalous problem in that they show a considerable difference in surface hardness. All the samples listed in Table XVI were (1) cut from the same bar, (2) treated in controlled atmosphere furnaces at the same time on the same tray, (3) all were quenched in oil at the same time, (4) all samples were double drawn at the same time. All samples had been prepared for hardening by grinding 0.045 inch from each of the broad test surfaces. After treating all samples were "gang" ground to clean surfaces and an additional 0.003 inch removed from the broad surfaces. As hardened and as nitrided one surface was face upward as placed on the tray for hardening and in the basket for nitriding. The top surfaces were tested for micro-hardness.

Sample "E" was repolished on the bottom side and tested for micro-hardness. Below is comparison of the micro-hardness numbers obtained on the two surfaces of sample "E":

	Hardness Numbers	
	1000-Gram Load	500-Gram Load
Top Side	755	744
	769	768
Bottom Side	778	769 (near edge)
Bottom Side	814	794 (near center)

The bottom side of sample "E" appears to be somewhat harder than the top side. A microscopic study of the indentation marks in samples "C" and "E" indicates "C" to be more brittle (or harder) than "E". The areas around the indentation marks on sample "C" show much more microscopic distortion or cracking than do the impressions on "E". See Figs. 8 and 9.

The high surface hardness induced in the surface of the annealed sample "M" by nitriding at 1050 degrees Fahr. for 31 minutes as indicated by the micro-indentation hardness is quite definitely supported by the micrograph, Fig. 13. This figure is a micrograph of a Rockwell "A" (60 Kg. load) impression at ×100 on the nitrided surface of sample "M". Note the radial and peripheral cracks in the hard surface around the Rockwell impression. The sinking of the hard case may be observed at the periphery of the jagged impression.

Table XVII

Micro-Indentation Hardness Numbers of Treated, Micro-Polished and Nitrided High Speed Steel Specimens. Variable Temperature—Constant Time Series. Bath Free from Nickel Contamination

Specimen No.	Nitrided 30 Min. Degrees Fahr.	Analysis of Bath Per Cent CN	Per Cent CNO	Repolishing After Nitriding	Rockwell C Scale	Micro-Indentation Hardness H for Loads in Grams 2000	1000	500	200	100
81	900	25.55	15.04	Broadcloth	64.0	830	860	868	905	900
83	950	25.17	14.73	Broadcloth	63.9	834	881	909	925	991
85	1000	24.44	14.48	Broadcloth	64.0	859	954	1012	1048	1044
87	1050	23.83	14.26	Broadcloth	64.0	908	959	1033	1070	1100
89	1100	23.63	14.28	Canvas and Broadcloth	63.8	963	1027	1044	1020	1030

Table XVIII

Micro-Indentation Hardness Numbers of Annealed, Micro-Polished and Nitrided High Speed Steel Specimens. Constant Temperature—Variable Time Series. Bath Free from Nickel Contamination. Cyanogen (CN) 23 to 25 Per Cent

Sample No.	Nitrided 1050° F.	Repolishing After Nitriding	Rockwell A Scale	Micro-Indentation Hardness Numbers H for Loads in Grams 2000	1000	500	200	100	50
70	11 min.	Broadcloth	60.0	307	373	457	572	667	748
71	31 min	Broadcloth	59.8	363	455	583	752	778	753
72	61 min.	Broadcloth	59.8	449	584	704	829	855	811
73	121 min.	Canvas and Broadcloth	59.8	610	725	850	826	768	...
74	181 min.	Canvas and Broadcloth	60.0	718	765	768	698	647	...
75	241 min.	Canvas and Broadcloth	59.6	737	765	727	650	600	...
76	301 min.	Canvas and Broadcloth	59.5	717	701	654	596	552	...

Table XIX

Micro-Indentation Hardness Numbers of Hardened, Double Drawn, Micro-Polished and Nitrided High Speed Steel Specimens. Samples Run Concurrently with Annealed Specimens of Table XVIII

Sample No.	Nitrided 1050° F.	Repolishing After Nitriding	Rockwell C Scale	Micro-Indentation Hardness Numbers H for Loads in Grams 2000	1000	500	200	100
90	11 min.	Broadcloth	63.7	833	871	898	947	996
91	61 min.	Broadcloth	64.0	970	1042	1042	1080	....
92	121 min.	Broadcloth	64.2	1018	1062	1067	1097	....
93	181 min.	Canvas and Broadcloth	64.0	1057	1097	1102	1114	....
94	241 min.	Canvas and Broadcloth	63.8	1067	1095	1097	1081	....

Table XX

Micro-Indentation Hardness Numbers of Treated, Micro-Polished and Electrically Insulated Nitrided Specimens. Constant Temperature—Variable Time Series. Bath Free from Nickel Contamination. Cyanogen (CN) of Bath 23 to 25 Per Cent

Sample No.	Nitrided 1050° F.	Repolishing After Nitriding	Rockwell C Scale	Micro-Indentation Hardness Numbers H for Loads in Grams 2000	1000	500	200	100
100	11 min.	Broadcloth	63.5	851	917	938	999	1032
101	31 min.	Broadcloth	63.6	956	976	1014	1050	1090
102	61 min.	Broadcloth	63.0	965	1004	1042	1132	1132
103	121 min.	Broadcloth	63.1	1048	1079	1093	1109	1122
104	181 min.	Broadcloth	63.0	1043	1064	1080	1085	1157

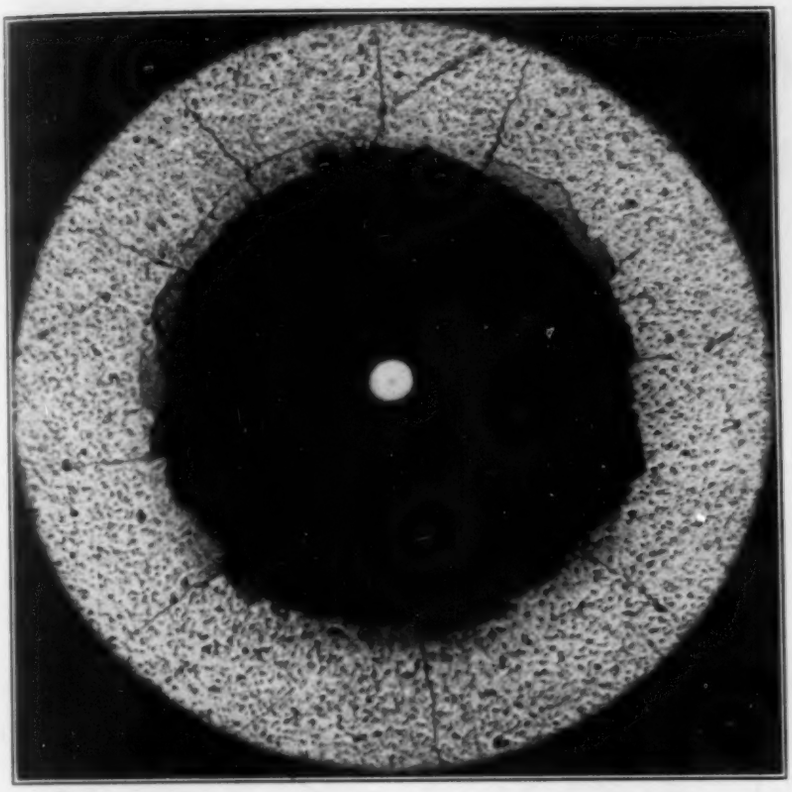


Fig. 13—Rockwell A Impression on the Surface of a Sample of Annealed, Polished and Nitrided High Speed Steel. Sample Nitrided at 1050 Degrees Fahr. for 31 Minutes. Unetched. × 100.

Table XVII is a tabulation of the micro-indentation numbers of various samples nitrided for 30 minutes at 900 to 1100 degrees Fahr. in 50-degree Fahr. increments. A temperature of 1050 degrees Fahr. for 30 minutes appears to produce the highest surface hardness. The surface hardness of the 1100-degree Fahr. sample is less than that of the 1050-degree Fahr. sample, although the depth of hardness penetration is greater. Fig. 14 shows the curves developed by plotting the nitriding temperatures (constant immersion time) against the micro-indentation hardness of the surface.

Table XVIII shows the effect on the surface hardness due to nitriding annealed and micro-polished specimens at 1050 degrees Fahr. for various periods of time. There is a progressive increase in hardness penetration as shown by the hardness numbers obtained at 2000-gram loads. The maximum surface hardness appears to be attained in 61 minutes. There is a progressive decrease in hardness from 61 minutes to 300 minutes as shown by the numbers obtained at 100-gram loads. Fig. 15 shows the curves generated on the an-

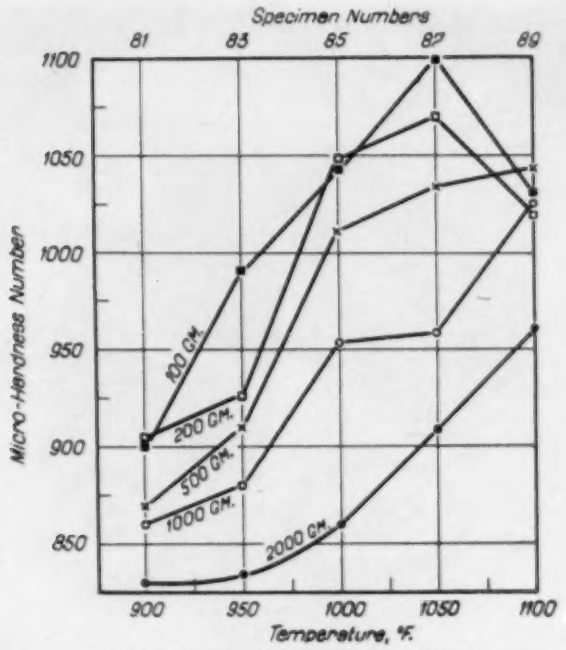


Fig. 14—Micro-Indentation Hardness of Hardened High Speed Steel After Nitriding for 30 Minutes at Various Temperatures.

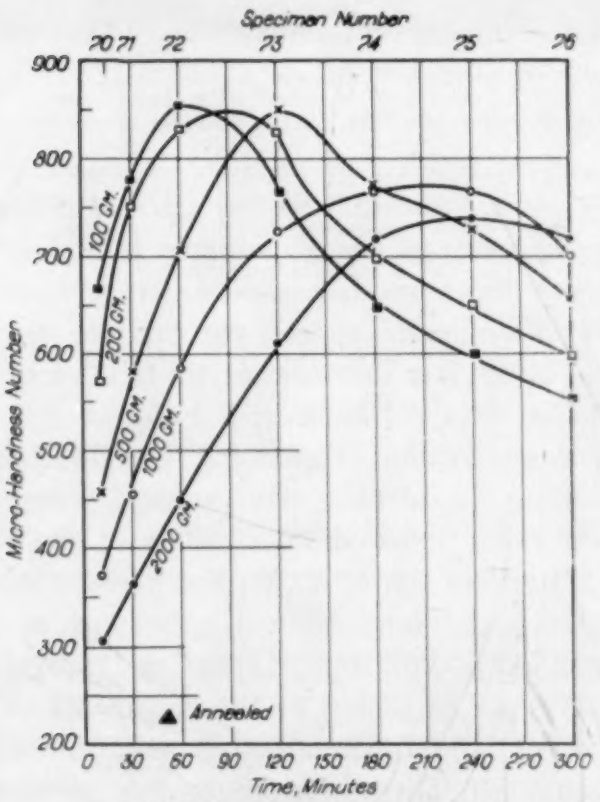


Fig. 15—Micro-Indentation Hardness of Annealed and Micro-Polished High Speed Steel After Nitriding at 1050 Degrees Fahr. for Various Times.

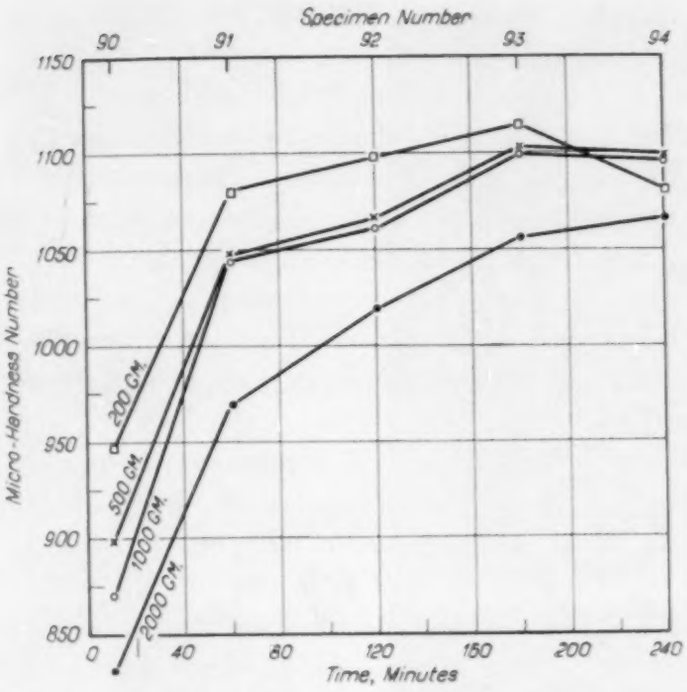


Fig. 16—Micro-Indentation Hardness of Hardened High Speed Steel Nitrided at 1050 Degrees Fahr. for Various Periods of Time.

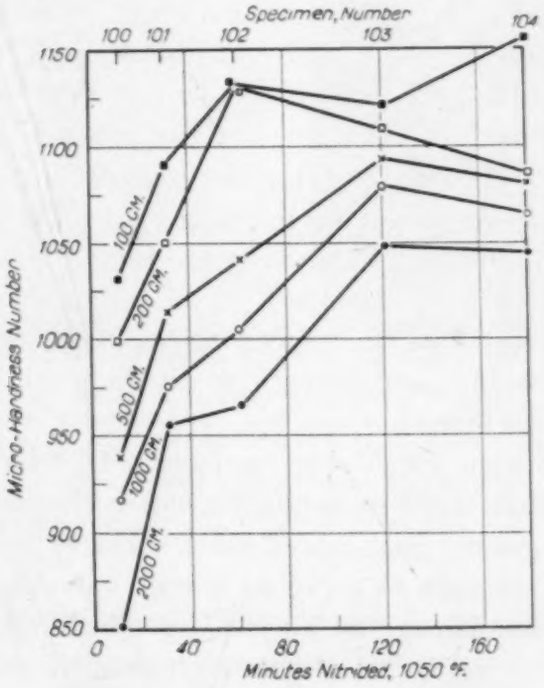


Fig. 17—Micro-Indentation Hardness of Treated and Nitrided High Speed Steel Electrically Insulated During Nitriding.

nealed and nitrided specimens plotting the nitriding time against the micro-hardness number.

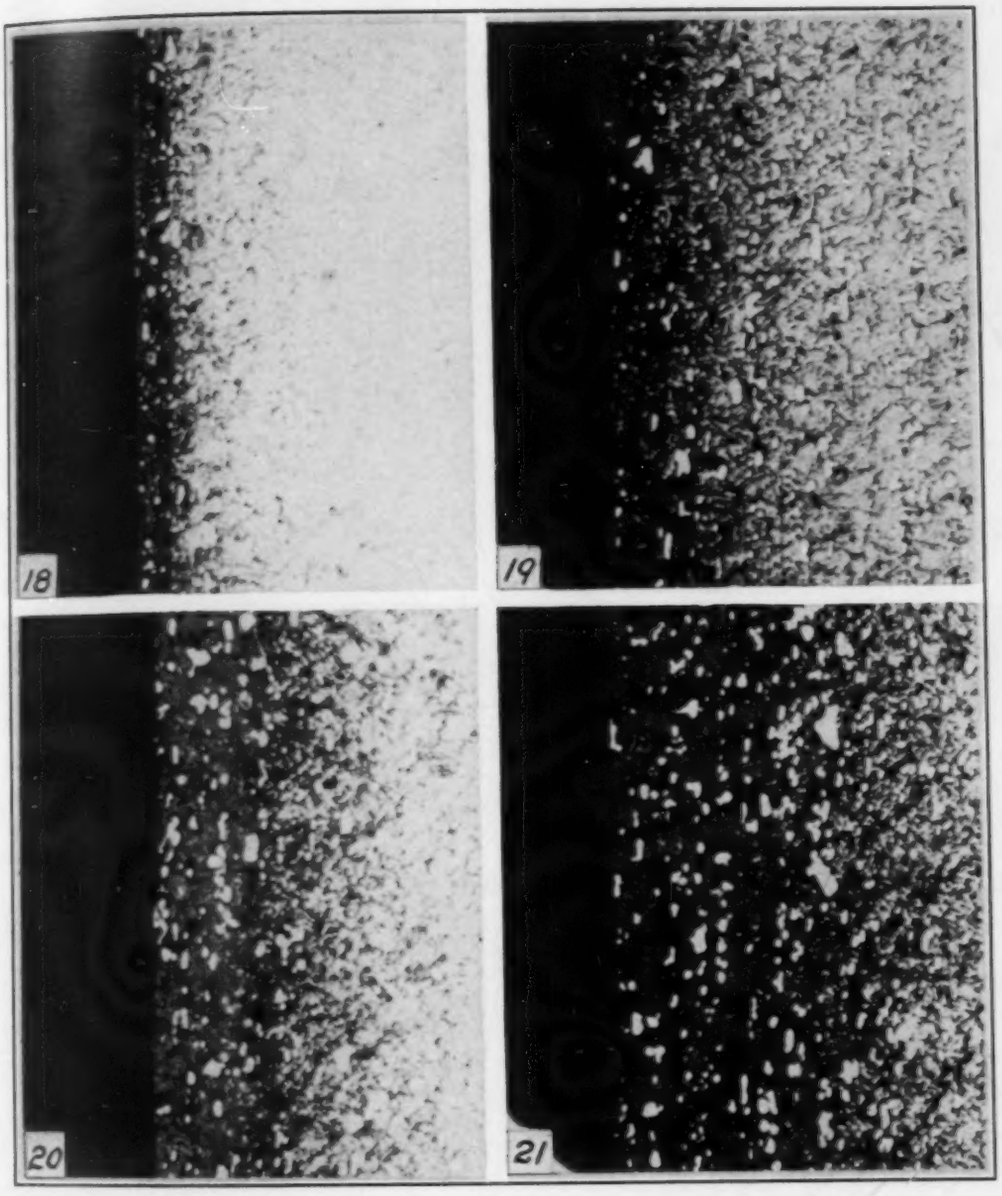
Table XIX shows the influence of time on the micro-hardness of fully treated and micro-polished specimens nitrided at 1050 degrees Fahr. for various periods of time. There is little difference in hardness at 200-gram loads between a 61-minute period of immersion and 180 and 240-minute periods. A progressive increase in the depth of hardness penetration is indicated at 2000-gram loads as the time of immersion is increased. Fig. 16 shows the curves obtained by plotting the time of immersion against the hardness numbers given in Table XIX.

Table XX shows the effect on surface hardness due to electrically insulating fully treated high speed steel during nitriding at 1050 degrees Fahr. These specimens were all prepared for the hardness testing after nitriding by a light polishing on the final broadcloth polishing wheel. The surfaces of all specimens as nitrided showed little difference as regards microscopic pitting. In Fig. 17 the time of immersion at 1050 degrees Fahr. is plotted against the hardness numbers at various loads for the samples listed in Table XX.

The nitriding of a decarburized high speed steel surface should be avoided. High speed steel which has been heated for hardening in salt baths or other media under conditions which tend to cause decarburization should preferably not be quenched in salt baths for hardening which contain cyanides. In the case of high speed steel the nitriding of a decarburized surface results in a brittle surface condition similar to that observed in the case of nitrided decarburized surfaces of the Nitralloy Steels. Fig. 13 which shows the sinking and cracking of the nitrided surface of an annealed high speed steel sample under a Rockwell A impression will illustrate the sinking which would probably accompany the nitriding of a decarburized high speed steel surface.

Nitriding of high speed steel surfaces which have been decarburized accomplishes little in a positive corrective way. However, the nitriding of ground high speed steel surfaces which have been abusively ground appears to serve as a very valuable corrective for at least some of the damage which may have been done in grinding.

8. *The Microstructure.* The measurement of the nitrided cases is a somewhat difficult problem. As etched in 4 per cent nital a section of a nitrided case will show a more or less darkening of the outer or nitrided zone. This generally grades gradually into the



Figs. 18 and 19—Photomicrographs Showing the Variation in Apparent Nitrided Case Depth Due to Short Etching Time and an Etching Time which Develops the Structure of the Core. Sample 86. Fig. 18 Light Etch. Fig. 19 Normal Etch. 4 Per Cent Nital. × 500.

Figs. 20 and 21—Photomicrographs Showing the Variation in Apparent Nitrided Case Depths Due to Short Etching Time and an Etching Time Which Develops the Structure of the Core. Sample 104. Fig. 20 Light Etch. Fig. 21 Normal Etch. 4 Per Cent Nital. × 500.

lighter color of the core. The microscopic measurement is somewhat similar to the measurement of the case of a carburized steel, in which we may measure (1) the hyper and eutectoid zones or (2) the case to the depth containing approximately 0.50 per cent carbon or (3) the total depth of case. It is further complicated, however,

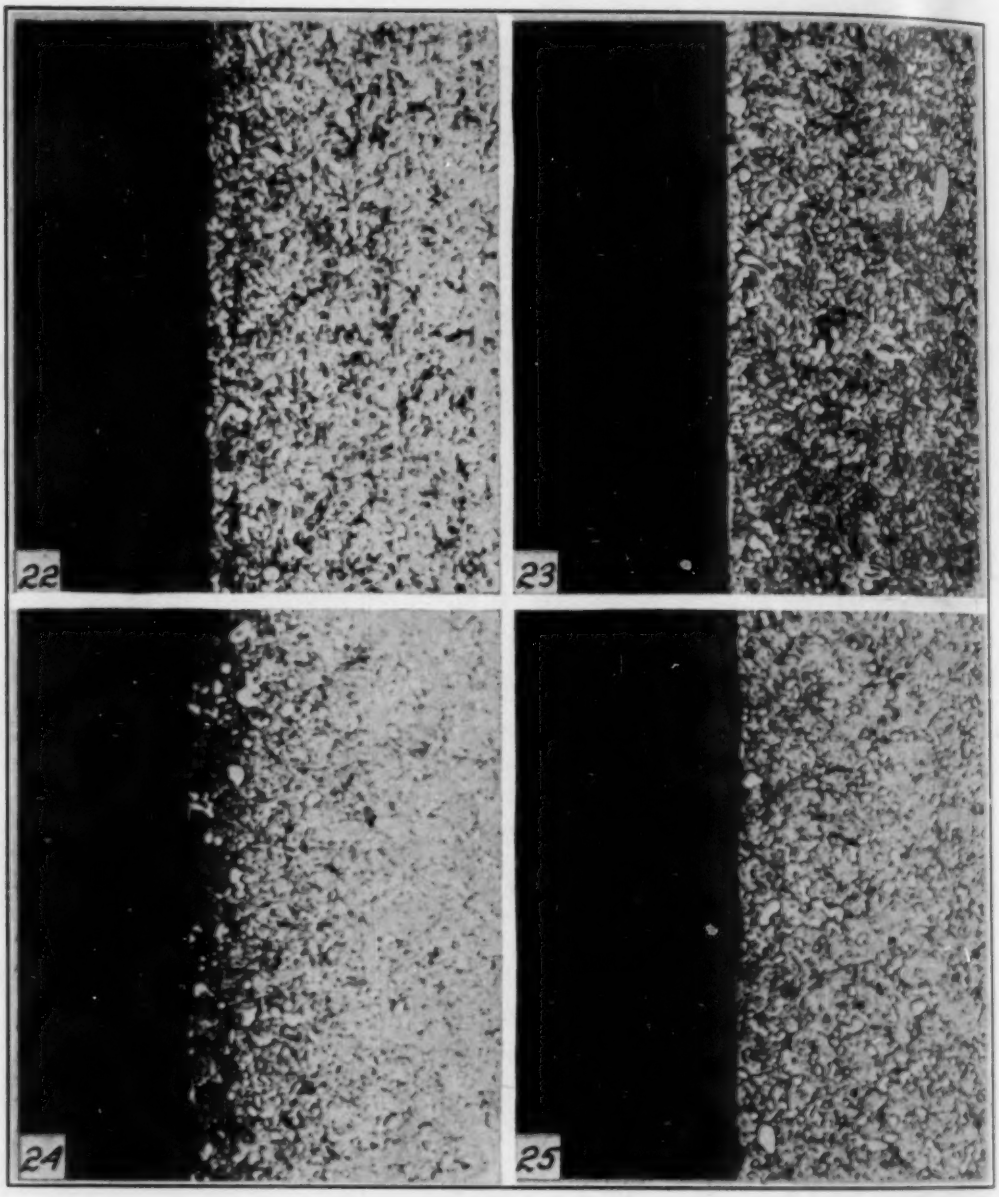


Fig. 22—Sample No. 1. Nitrided 850 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 23—Sample No. 2. Same Heating Cycle as Sample No. 1. Not Nitrided. Etchant 4 Per Cent Nital. × 500.
Fig. 24—Sample No. 3. Nitrided 950 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 25—Sample No. 4. Same Heating Cycle as Sample No. 3 But Not Nitrided. Etchant 4 Per Cent Nital. × 500.

by the fact that the case of a nitrided high speed steel usually shows no structural gradation but only a color gradation. The case measurements here presented are therefore at best an estimation of the depth based on the darker color which develops on etching a nitrided case in 4 per cent nital. It is difficult to duplicate the same depth of

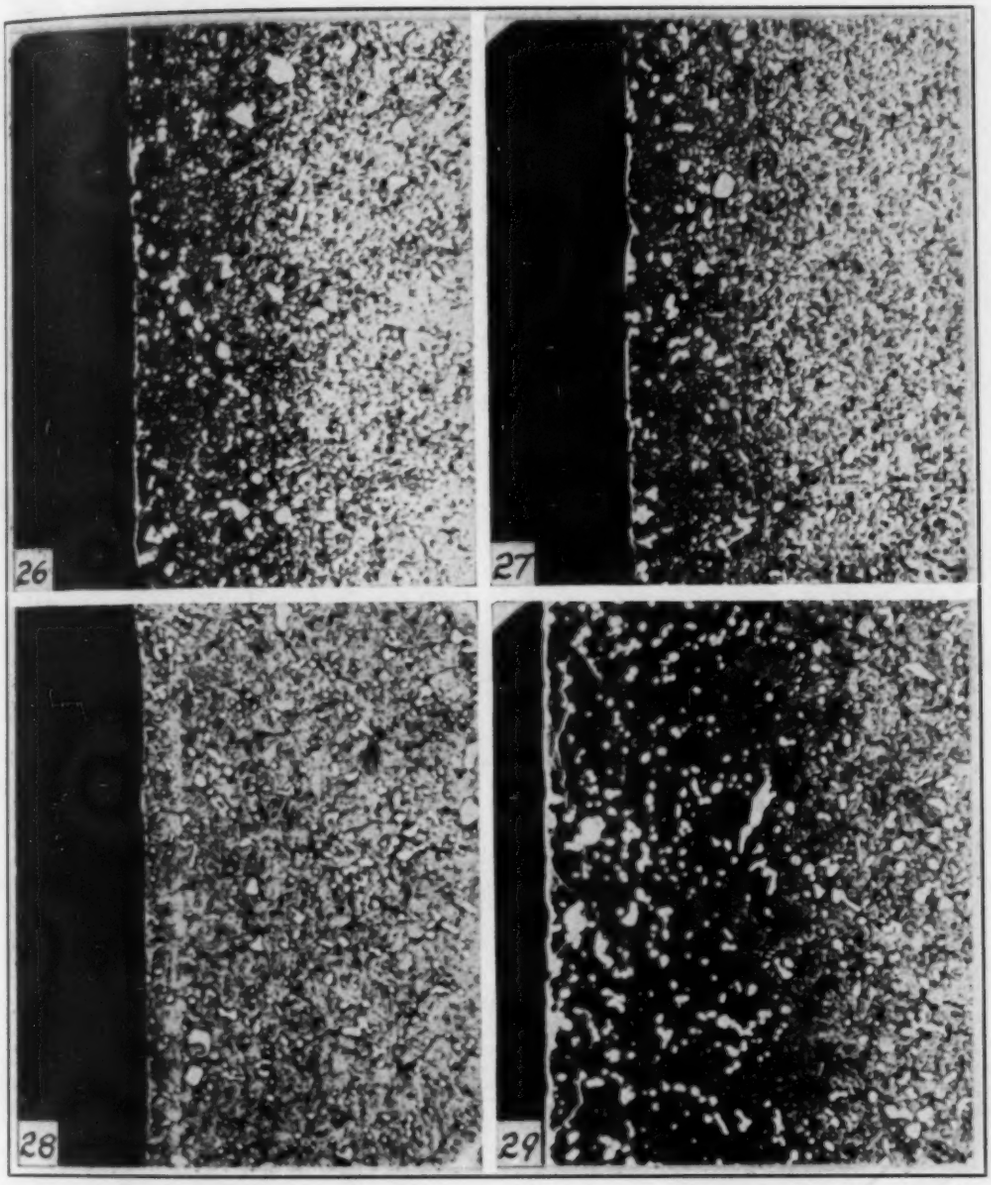


Fig. 26—Sample No. 21. Preheated 1050 Degrees Fahr. Nitrided 1000 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 27—Sample No. 19. Nitrided 1000 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 28—Sample No. 10. Same Heating Cycle as Sample No. 19 But Not Nitrided. Etchant 4 Per Cent Nital. × 500.
Fig. 29—Sample No. 5. Nitrided 1150 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. Note Nickel Plate on Surface. × 500.

case or same color differences on repolishing and re-etching the same sample. The depth of case may vary due to one's judgment as to the color line; also the color difference appears to be sensitive to etching time, etchant concentration and possibly differential surface oxidation after polishing and prior to etching. No investiga-

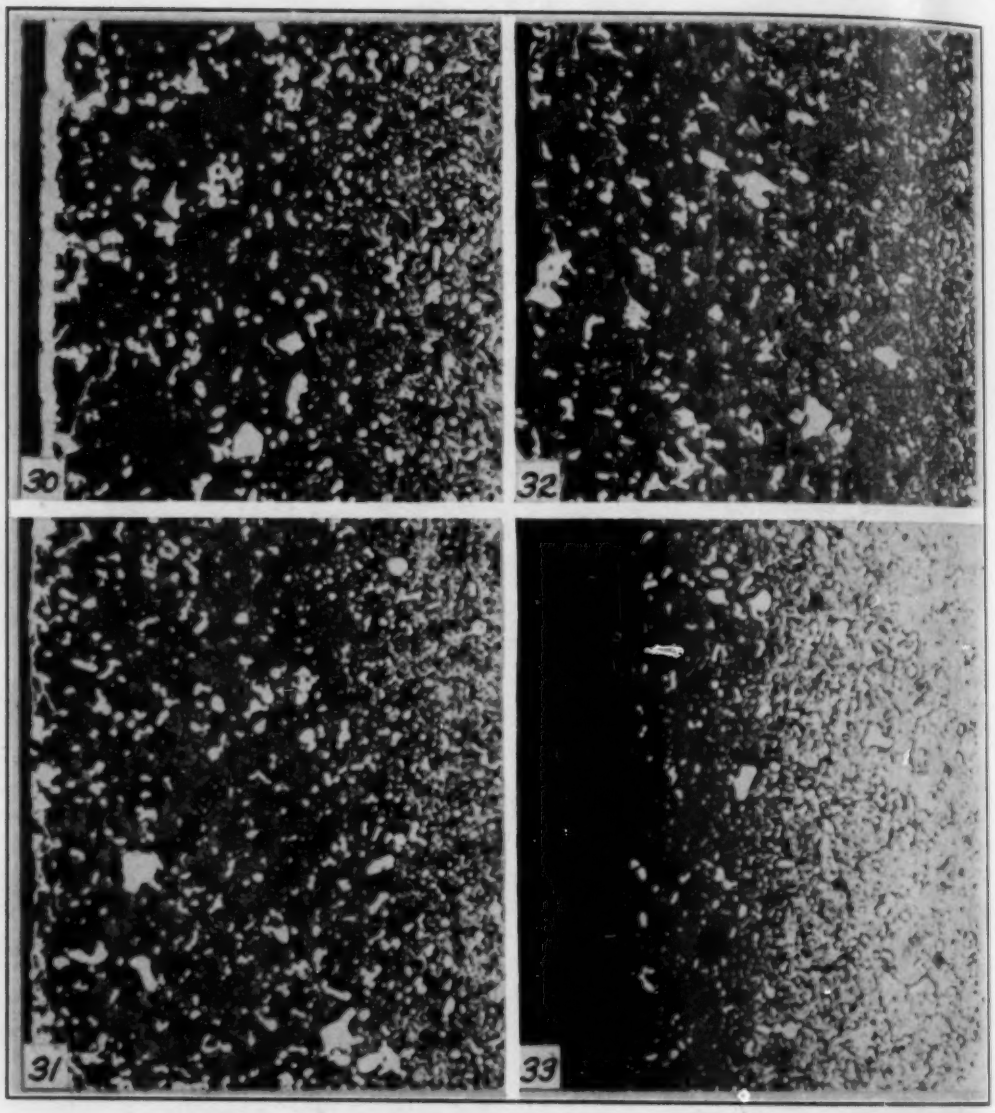


Fig. 30—Sample No. 11. Nitrided 1250 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. Note Nickel Plate on Surface. × 500.
Fig. 31—Sample No. 22. Nitrided 1050 Degrees Fahr. for 180 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 32—Sample No. 23. Nitrided 1050 Degrees Fahr. for 360 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 33—Sample No. 15. Nitrided 1050 Degrees Fahr. for 30 Minutes in a Freshly Prepared 60-40 Mixture. Etchant 4 Per Cent Nital. × 500.

tion of etching reagents was attempted. It is possible a better etchant may be developed. The case as measured by etching in 4 per cent nital is not a measure of the nitrogen penetration. For example—micro sample No. 3 of Table XIV appears to show a case depth of 0.0005 inch whereas the nitrogen analysis of the cut 0.001 to 0.002 inch shows a nitrogen content of five times that of the steel itself.

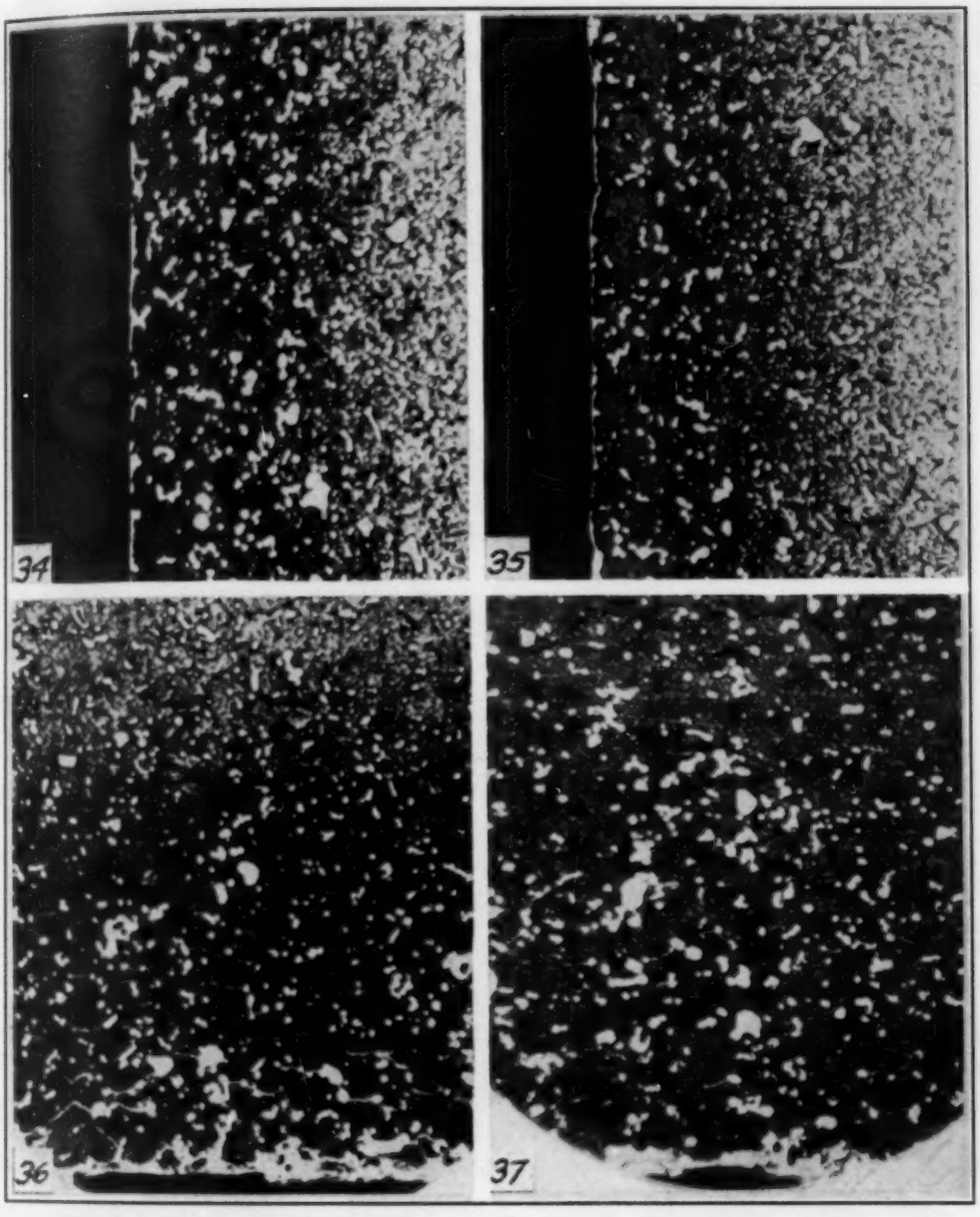


Fig. 34—Sample No. 18. Nitrided 1050 Degrees Fahr. for 90 Minutes in a Freshly Prepared 60-40 Mixture. Etchant 4 Per Cent Nital. × 500.
Fig. 35—Sample No. 8. Nitrided 1050 Degrees Fahr. for 90 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 36—Sample No. 7. Nitrided 16 Hours Between 825 and 1175 Degrees Fahr. Etchant 4 Per Cent Nital. × 500.
Fig. 37—Sample No. 24. Nitrided at Same Time as Sample No. 7. Etchant 4 Per Cent Nital. × 500.

Micrographs (Figs. 29, 30 and 36) of samples No. 5, No. 11 and No. 7 nitrided respectively at 1150 degrees Fahr. for 30 minutes, 1250 degrees Fahr. for 30 minutes and for 16 hours between 825 and 1175 degrees Fahr. show a remnant grain outline close to the surface. This probably does not represent a change in structure but rather,

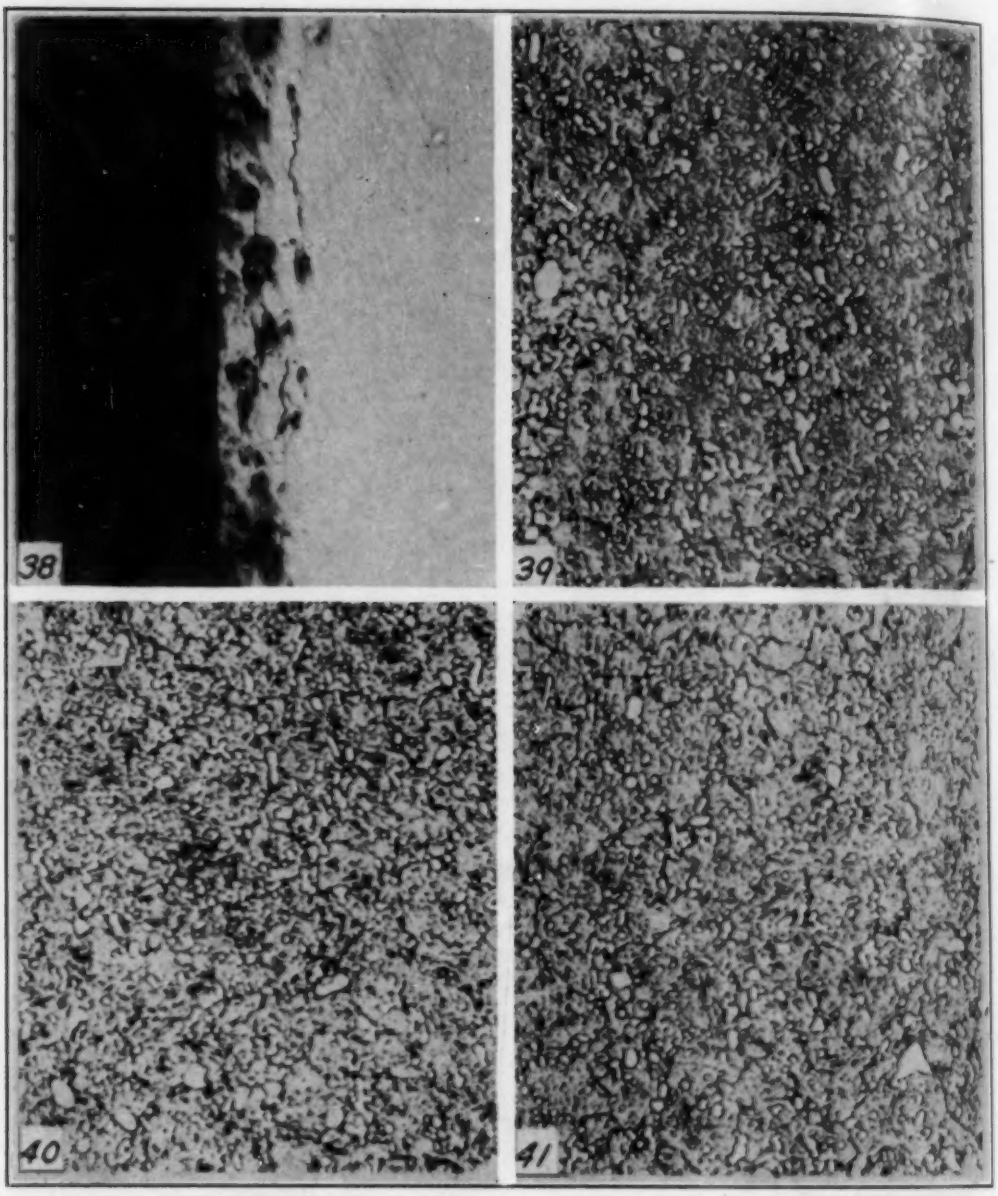


Fig. 38—Sample No. 24. Unetched. × 500.
Fig. 39—Sample No. 11. Etching Time 1 Minute. Etchant 4 Per Cent Nital. Body Structure—Quenched 2350 Degrees Fahr., Tempered 1080 Degrees Fahr. Nitrided 1250 Degrees Fahr. for 30 Minutes. × 500.
Fig. 40—Sample No. 18. Etching Time 2 Minutes 15 Seconds. Etchant 4 Per Cent Nital. Body Structure—Quenched 2350 Degrees Fahr., Tempered 1080 Degrees Fahr. Nitrided 1030 to 1070 Degrees Fahr. for 90 Minutes. × 500.
Fig. 41—Sample No. 24. Etching Time 2 Minutes 45 Seconds. Etchant 4 Per Cent Nital. Body Structure—Quenched 2350 Degrees Fahr., Tempered 1080 Degrees Fahr. Nitrided 16 Hours at Temperature Between 825-1200 Degrees Fahr. × 500.

we believe, delineates partially the austenitic grain boundaries due to the differential etching effect induced by the absorbed nitrogen.

Specimens No. 7, No. 8, No. 18, No. 19, No. 21 and No. 22 (Figs. 36, 35, 34, 27, 26 and 31 respectively) show a discontinuous

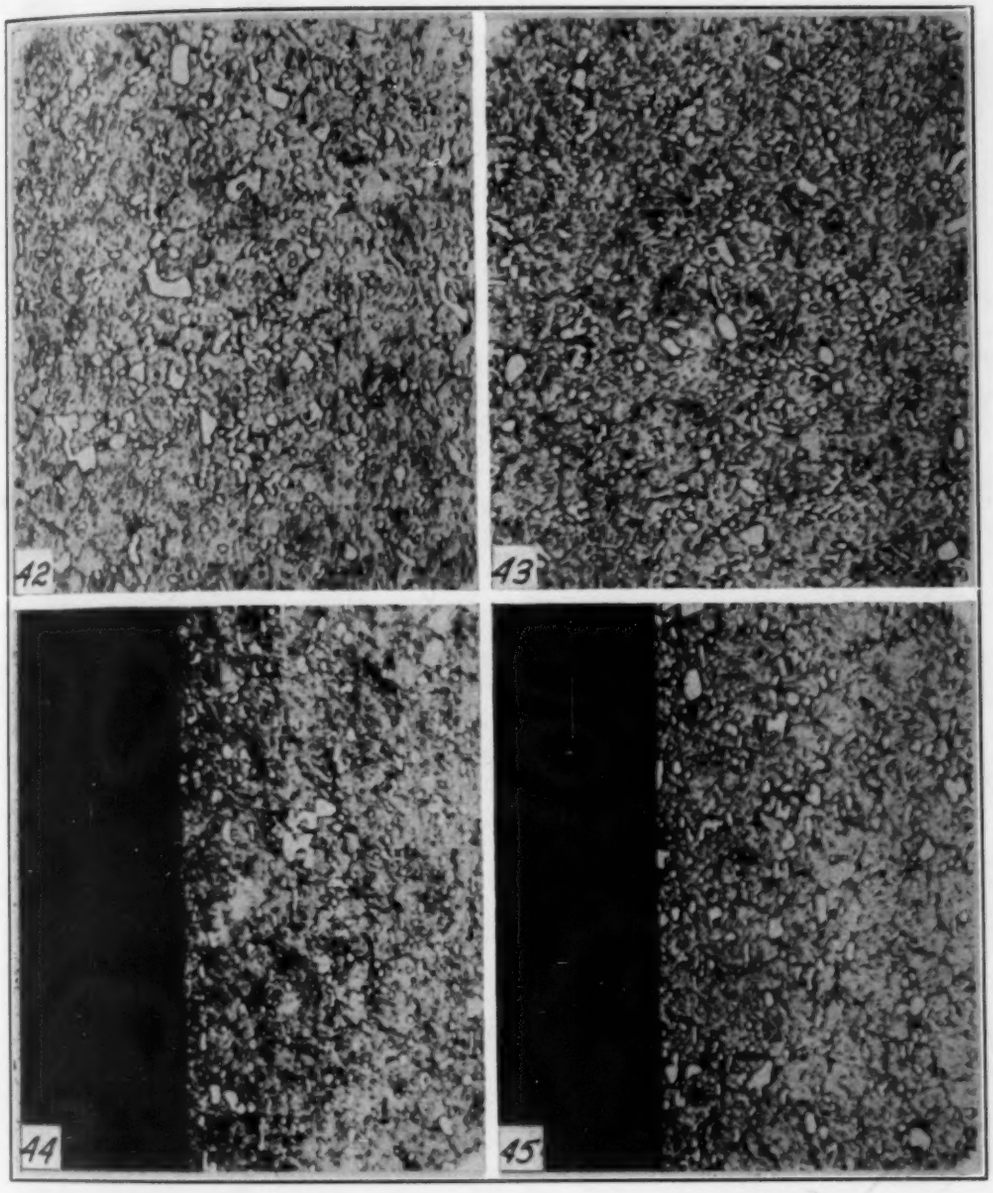


Fig. 42—Sample No. 5. Etching Time 1 Minute 30 Seconds. Etchant 4 Per Cent Nital. Body Structure—Quenched 2350 Degrees Fahr., Tempered 1080 Degrees Fahr. Nitrided 1150 Degrees Fahr. for 30 Minutes. × 500.

Fig. 43—Sample No. 8. Etching Time 2 Minutes 30 Seconds. Etchant 4 Per Cent Nital. Body Structure—Quenched 2350 Degrees Fahr., Tempered 1080 Degrees Fahr. Nitrided 1050 Degrees Fahr. for 90 Minutes. × 500.

Fig. 44—Sample No. 81. Treated High Speed Steel. Nitrided 900 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.

Fig. 45—Sample No. 83. Treated High Speed Steel. Nitrided 950 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.

white rim. Specimens No. 5, No. 11 and No. 7 (Figs. 29, 30 and 36) show continuous white rims. Sample No. 11 (Fig. 30) has a white rim approximately 0.00012 inch thick. The white discontinuous rims might be mistaken for carbides. Sample No. 11 appears

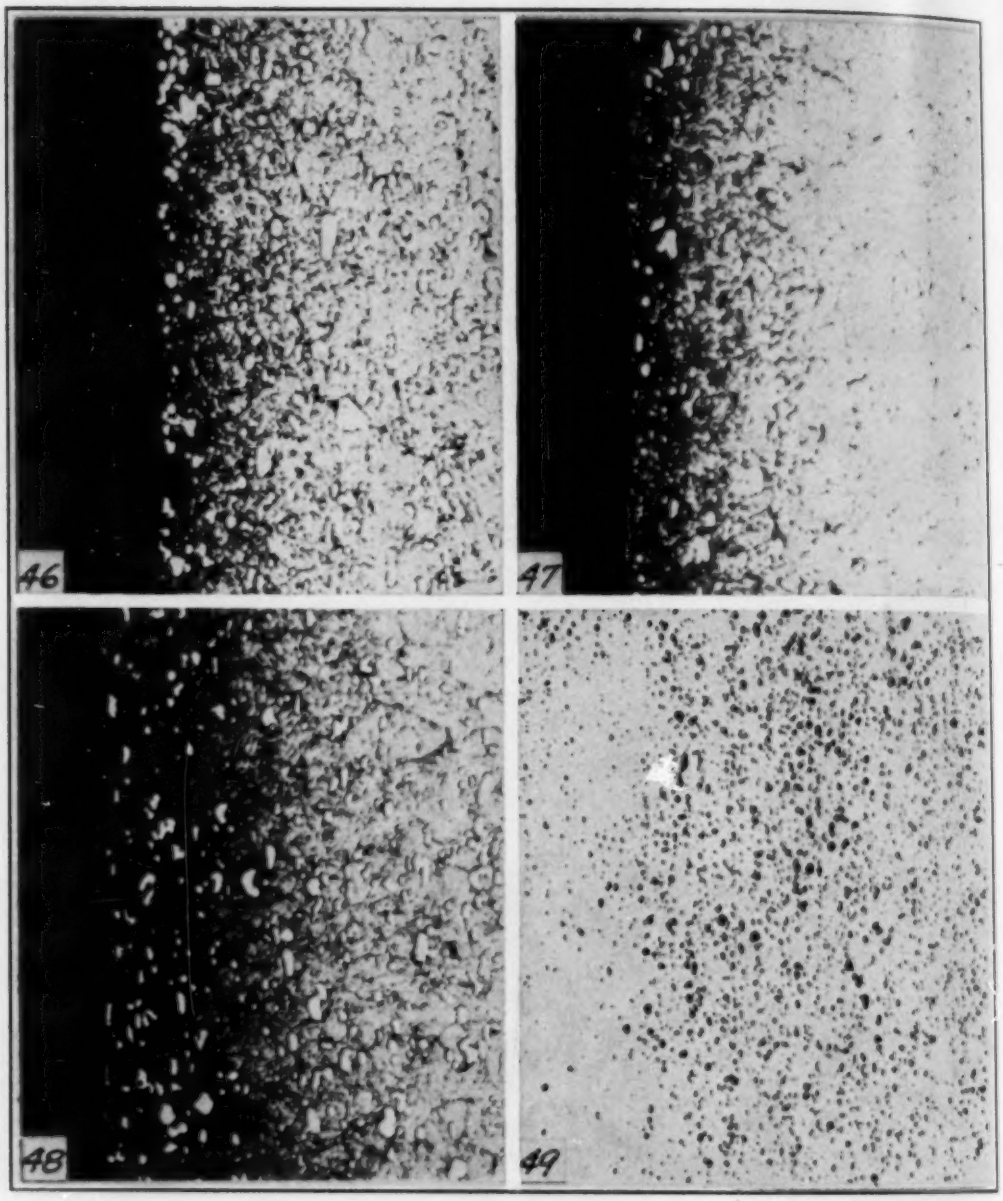


Fig. 46—Sample No. 85. Treated High Speed Steel. Nitrided 1000 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 47—Sample No. 87. Treated High Speed Steel. Nitrided 1050 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 48—Sample No. 89. Treated High Speed Steel. Nitrided 1100 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 49—Sample No. 87. Surface of Micro-Polished and Nitrided High Speed Steel. Nitrided 1050 Degrees Fahr. for 30 Minutes. Unetched. × 200.

quite obviously to be of the nature of a plate. This outer white zone is practically pure nickel which was plated onto the surface during nitriding, due to the bath being contaminated with nickel.

Etched sample No. 18 (Fig. 34) shows a discontinuous white rim. This sample was nitrided in a freshly prepared 60-40 mix-

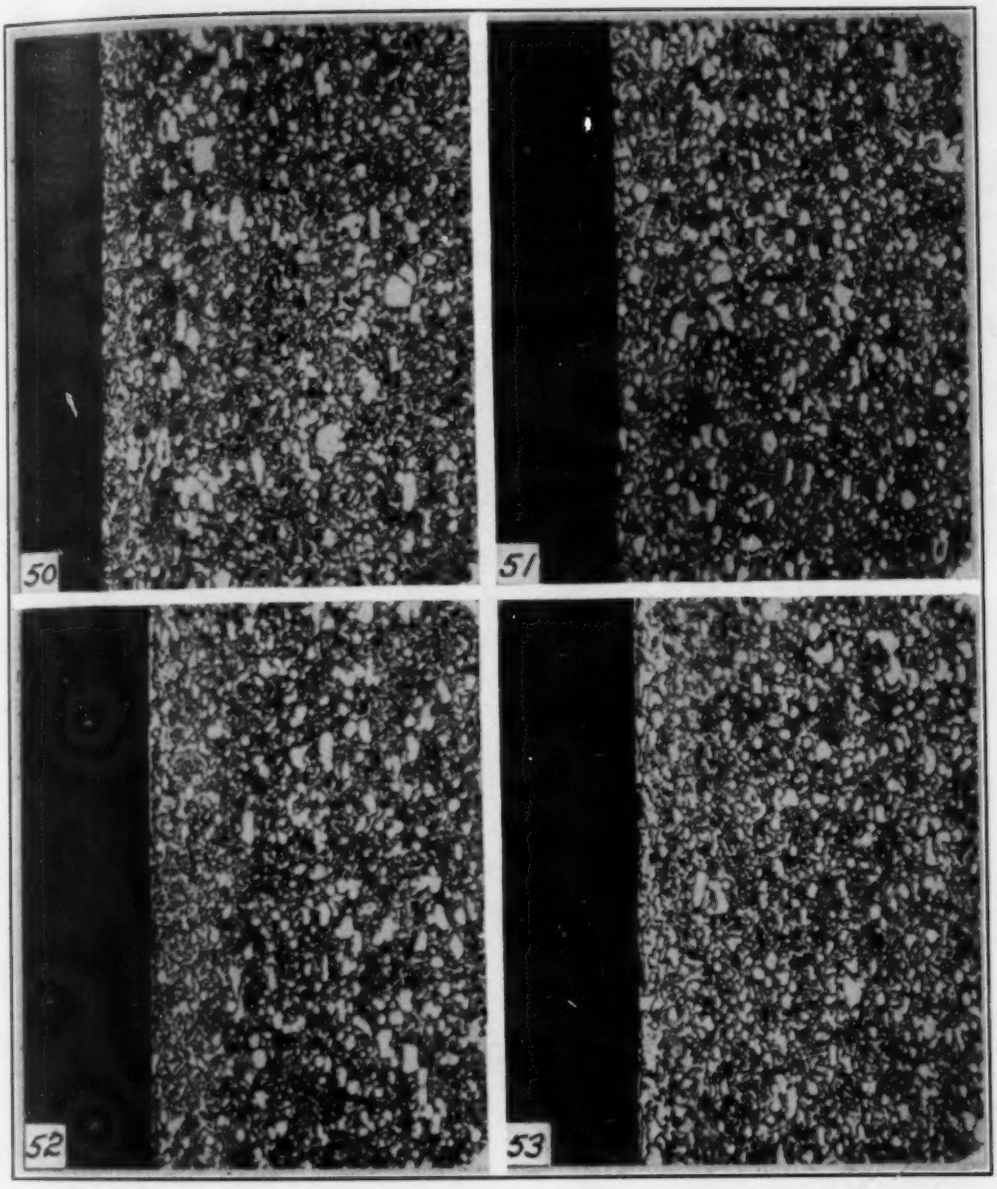


Fig. 50—Sample No. 95. Annealed High Speed Steel. Nitrided 900 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 51—Sample No. 96. Annealed High Speed Steel. Nitrided 950 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 52—Sample No. 97. Annealed High Speed Steel. Nitrided 1000 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.
Fig. 53—Sample No. 98. Annealed High Speed Steel. Nitrided 1050 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.

ture contained in a pressed steel pot. The bath became contaminated with nickel due to the use of a pure nickel thermocouple protection tube.

The nitrided cases of samples No. 5 and No. 8 (Figs. 29 and 35) show a lighter colored etched outer zone merging into a darker

zone and the latter grading into the lighter colored core zone. This may be of some significance when reference is made to the humps in the micro-hardness gradient curves of Fig. 12. The curve for sample No. 8 shows an increase in hardness number of 860 to 900 between a depth of 0.000590 inch (15 μ) and 0.001141 inch (29 μ) which compares with 0.000626 inch, the depth of the lighter colored outer dark zone of micrograph (Fig. 45) and 0.001 inch the approxi-

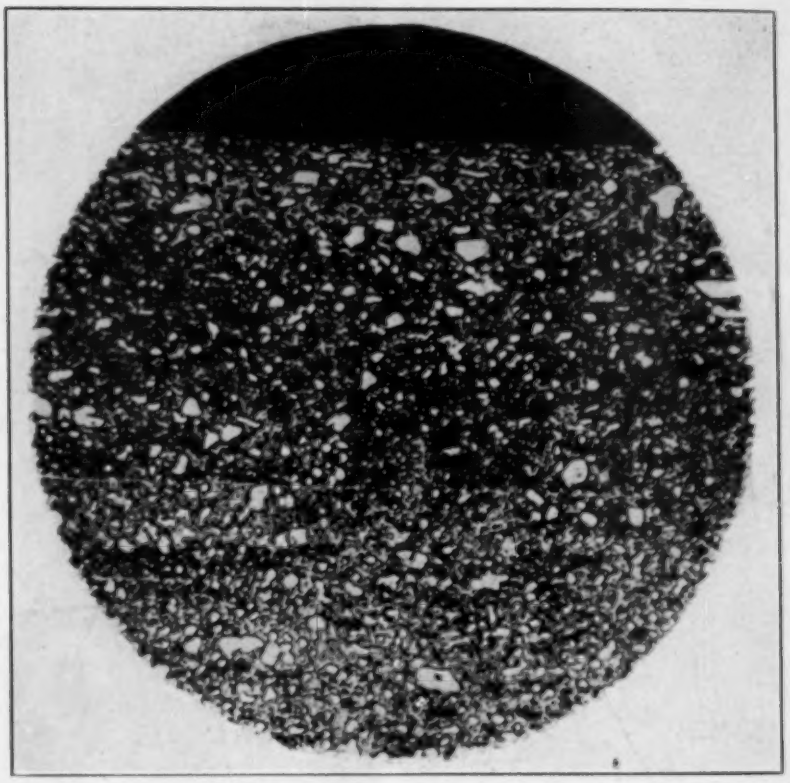


Fig. 53A—Sample No. 99. Annealed High Speed Steel. Nitrided 1100 Degrees Fahr. for 30 Minutes. Etchant 4 Per Cent Nital. × 500.

mate depth of the darkest area of the dark center zone. However, the micrographs of samples No. 22 and No. 23 (Figs. 31 and 32) do not show the lighter colored outer zone.

Curiosity samples No. 7 and No. 24 (Figs. 36 and 37) which were nitrided for 16 hours show on the top sides after nitriding a crumbly brittle layer of 0.0002 inch in thickness. This could be chipped off by means of a sharp pointed tool. It appeared to be a built-up surface rather than a part of the high speed steel. Having learned that a cyanide bath may contain a small amount of nickel which may plate onto the surface of immersed high speed steel it

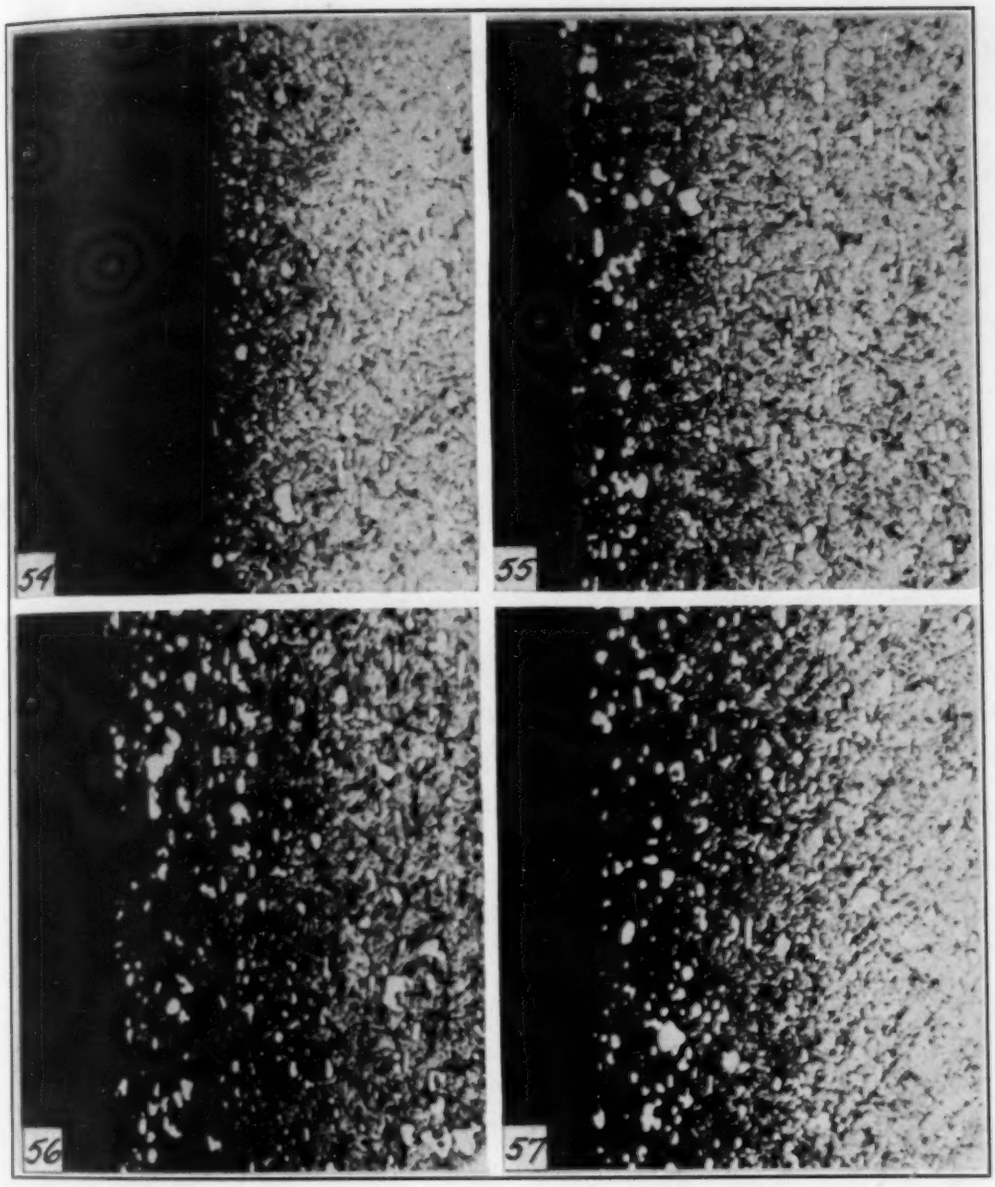


Fig. 54—Sample No. 100. Treated High Speed Steel. Nitrided 1050 Degrees Fahr. for 11 Minutes. Electrically Insulated During Nitriding. Etchant 4 Per Cent Nital. × 500.

Fig. 55—Sample No. 101. Treated High Speed Steel. Nitrided 1050 Degrees Fahr. for 31 Minutes. Electrically Insulated During Nitriding. Etchant 4 Per Cent Nital. × 500.

Fig. 56—Sample No. 102. Treated High Speed Steel. Nitrided 1050 Degrees Fahr. for 61 Minutes. Electrically Insulated During Nitriding. Etchant 4 Per Cent Nital. × 500.

Fig. 57—Sample No. 103. Treated High Speed Steel. Nitrided 1050 Degrees Fahr. for 120 Minutes. Electrically Insulated During Nitriding. Etchant 4 Per Cent Nital. × 500.

was decided to check the matter of nickel contamination of the bath. One-half of sample No. 24, Table XIV, was dried and weighed on an analytical balance and then immersed in cold 25 per cent HNO_3

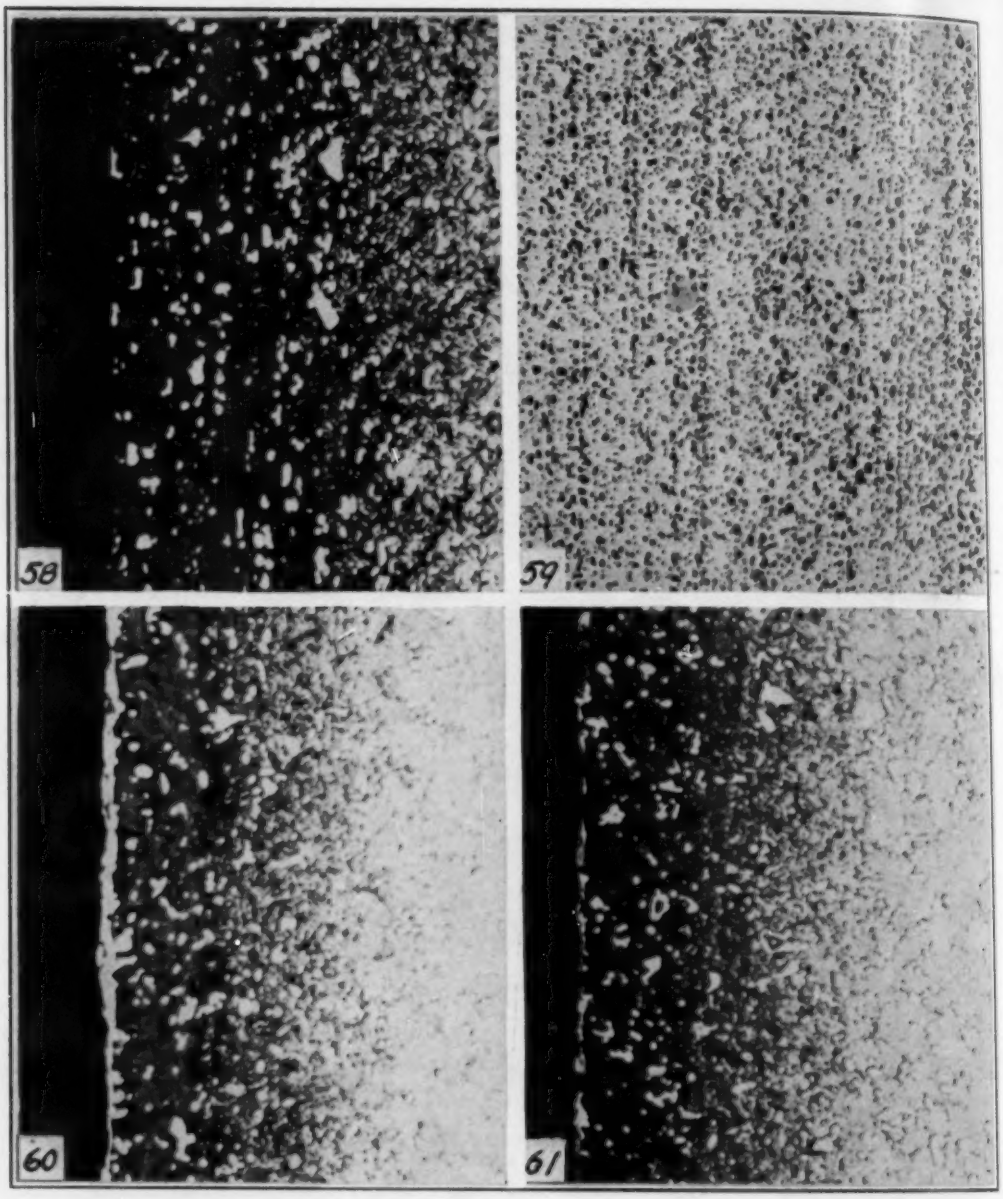


Fig. 58—Sample No. 104. Treated High Speed Steel. Nitrided 1050 Degrees Fahr. for 180 Minutes. Electrically Insulated During Nitriding. Etchant 4 Per Cent Nital. × 500.

Fig. 59—Sample No. 100. Surface After Nitriding. Unetched. × 200.

Fig. 60—Sample No. 40. Hardened and Ground High Speed Steel. Nickel Plated and Nitrided 1050 Degrees Fahr. for 120 Minutes. Nickel Plate 0.00002 Inch Thick. Etchant 4 Per Cent Nital. × 500.

Fig. 61—Sample No. 41. Same as Sample No. 40 Except Plated with Nickel to 0.00003 Inch Thickness Before Nitriding. Etchant 4 Per Cent Nital. × 500.

for about 20 minutes. It was observed that shortly after chemical attack of the surface had started, the surface became jet black in color suggestive of carbon which may have been trapped by the deposited nickel. The sample was then removed after rubbing with a rubber policeman and washing with distilled water. The sample

was again dried and weighed. The difference in weight represented the weight of the analytical sample. Analyzed for nickel the striped nitrided surface showed 3.83 per cent nickel. The analysis together with the evidence shown in the micrograph of Fig. 37 indicates a rather pure plate of nickel of 0.0002 inch in thickness. Fig. 38 shows a distintegrated surface about 0.0007 inch in depth.

Figs. 44 to 48 inclusive show the etched edges of sectioned samples ⅜x½x1 inch which were nitrided concurrently with the analytical samples listed in Table X. Samples were treated and double drawn, then ground to remove 0.0003 inch of surface, micro-polished and then nitrided as designated under the micrographs.

Specimens No. 81 and No. 83 nitrided respectively at 900 and 950 degrees Fahr. show a faint darkening near the nitrided surface. Specimens nitrided at 1000, 1050 and 1100 degrees Fahr. show a progressive increase in apparent case depth as shown by the darker and deeper case.

Fig. 49 is a micrograph taken at ×200 of the surface of sample 87 nitrided at 1050 degrees Fahr. for 30 minutes. After nitriding, this specimen was repolished very lightly on the final broadcloth polishing wheel and then micrographed. The relatively clear area shown in the micrograph is a portion of the bright areas one often sees on nitrided surfaces.

Figs. 50 to 53 are micrographs of annealed high speed steel specimens ⅜x½x1 inch which were micro-polished and nitrided concurrently with the analytical samples of Table X. The micrographs of the annealed samples nitrided for 30 minutes at 900, 950. 1000 and 1050 degrees Fahr. show no evidence of change when etched in 4 per cent nital. The sample nitrided at 1100 degrees Fahr. shows a faint but inconclusive darkening of the outer zone.

Figs. 54 to 58 are micrographs taken at ×500 of ⅜x½x1-inch samples electrically insulated during nitriding at 1050 degrees Fahr. for various times from 11 minutes to 180 minutes. All specimens after nitriding were repolished lightly on the final broadcloth wheel only. There appeared to be little difference of the surface of electrically insulated samples which were nitrided 11 minutes and 180 minutes. Fig. 59 is a micrograph taken at ×200 of the nitrided surfaces of sample No. 100 which was given a light repolishing after nitriding. The etching pits shown in the micrograph of the specimen nitrided 11 minutes were only slightly smaller in diameter than the etching pits of specimen No. 104 which was nitrided 180 minutes.

9. *The Nature of the Surface as Regards Pitting, Nickel Plating, Appearance, etc.* The nitriding of ground high speed steel surfaces in molten cyanides is accompanied by a surface etching or microscopic pitting. This pitting, in the type of bath used in this investigation, has never been found detrimental since the depth of the pits is considerably less than the depth of grinding marks resulting from good commercial practice. At least this is true within the limits of time and temperature usually employed for nitriding high speed steel. The observed microscopic pitting occurs for the most part in the matrix on the carbide borders. The pitting does not tend to surround the carbides. The tendency for molten cyanide baths to attack a discontinuity existing in the container or thermocouple protection tube would suggest that a microstructural discontinuity would also be most vulnerable to attack.

The nitrided surfaces of hardened high speed steel which are free from nickel appear very resistant to attack by 25 per cent nitric acid when immersed in same. Surfaces containing nickel as a result of nitriding in a bath contaminated with nickel are quite readily attacked when immersed in 25 per cent nitric acid. When immersing surfaces containing nickel in the cold 25 per cent acid there is an avid attack in from 10 to 20 minutes with a rise in acid temperature due to the chemical action. Samples whose surfaces were free from nickel showed after 6 hours immersion practically no attack and consequently no rise in acid temperature.

To determine the effect of time and temperature as regards the etching or microscopic pitting of the steel surfaces by the bath a number of rectangular and round treated high speed steel samples were prepared. The steel used for this purpose had the following composition:

$\frac{1}{16}$-Inch Diameter

C	Mn	P	S	Si	Cr	V	Ni	W
0.71	0.23	0.016	tr.	0.31	3.93	1.03	0.078	17.88

$\frac{7}{16} \times 1\frac{1}{16}$ Inches

C	Mn	P	S	Si	Cr	V	Ni	W
0.685	0.21	0.021	tr.	0.33	3.99	0.97	0.07	17.84

A number of samples were rough machined to remove decarburization and treated as follows:

Preheat	—1550 degrees Fahr.
High Heat	—2350 degrees Fahr. Quench in oil
Drawn	—1080 degrees Fahr. 1¾ hours
Re-drawn	—1080 degrees Fahr. 1¾ hours
Rockwell C	—63.5

Table XXI

Weight Changes Resulting from Nitriding, Using Both An Aged and Freshly Prepared Bath with Nickel Alloy Pot

No.	Nitriding Minutes	Per Cent (CN) of Bath	Weight in Grams Before Nitriding	Weight in Grams After Nitriding	Change in Weight in Grams
30R	850° F.— 32	22.49	106.7583	106.7479	—0.0104
39R	850° F.— 32	21.85	107.5187	107.5025	—0.0162
40R	850° F.— 32	21.30	106.6802	106.6704	—0.0098
31R	950° F.— 32	21.36	107.3000	107.2982	—0.0018
32R	1050° F.— 12	21.30	107.5710	107.5694	—0.0016
33R	1050° F.— 32	21.30	106.6889	106.6870	—0.0019
34R	1050° F.— 92	20.75	106.6929	106.6787	—0.0142
35R	1050° F.—180	20.40	107.0536	107.0206	—0.0330
36R	1150° F.— 32	20.40	106.7349	106.7432	—0.0083
37R*	1055° F.— 12	44.55	107.8475	107.8427	—0.0048
38R*	1055° F.— 32	44.55	106.7319	106.7268	—0.0051
30C	850° F.— 32	22.49	126.5655	126.5538	—0.0117
31C	950° F.— 32	21.36	126.9140	126.9025	—0.0115
39C	950° F.— 32	21.36	126.4029	126.3896	—0.0133
32C	1050° F.— 12	21.30	126.5494	125.5425	—0.0069
33C	1050° F.— 32	21.30	126.4694	126.4643	—0.0051
34C	1050° F.— 92	20.75	126.3124	126.2999	—0.0125
40C	1050° F.— 92	20.75	125.7816	125.7575	—0.0241
35C	1050° F.—180	20.40	119.3775	119.3426	—0.0349
36C	1150° F.— 32	20.40	126.0744	126.0725	—0.0019
37C*	1055° F.— 12	44.55	126.4449	126.4390	—0.0059
38C*	1055° F.— 32	44.55	126.1144	126.1104	—0.0040

*Freshly prepared 60-40 mixture. Temperature ± 15 degrees Fahr.
Samples denoted R were rectangular—0.336x1.002x2.235 inches.
Samples denoted C were round—0.759 inch diameter x 1.985 inches long.

Table XXII

Results of Nickel Determinations Made on Samples Obtained by Stripping Surface of Nitrided Samples of Table XXI with Cold, 25 Per Cent Nitric Acid

Nos. Rectangular Samples	Nitriding	Wt. (Grams) Analytical Sample	Percentage Nickel in Sample	*Net Grams Nickel Added to Surfaces
30R	850° F. 32 min.	0.6618	0.070	None
31R	950° F. 32 min.	1.0459	0.32	0.0026
32R	1050° F. 12 min.	1.3268	0.105	0.00046
33R	1050° F. 32 min.	0.9709	0.21	0.0014
34R	1050° F. 92 min.	0.9896	0.72	trace
35R	1050° F. 3 hrs.	1.2449	0.187	0.00145
36R	1150° F. 32 min.	1.8307	0.164	0.0017
37R	1055° F. 12 min.	0.8963	0.084	0.00012
38R	1055° F. 32 min.	0.8348	0.090	0.00017
		Cylindrical Samples		
39C	950° F. 32 min.	0.4886	1.39	0.0065
40C	1050° F. 92 min.	0.6049	0.78	0.0043

*Obtained by subtracting the amount of nickel present in the high speed steel, in this case 0.07 per cent.

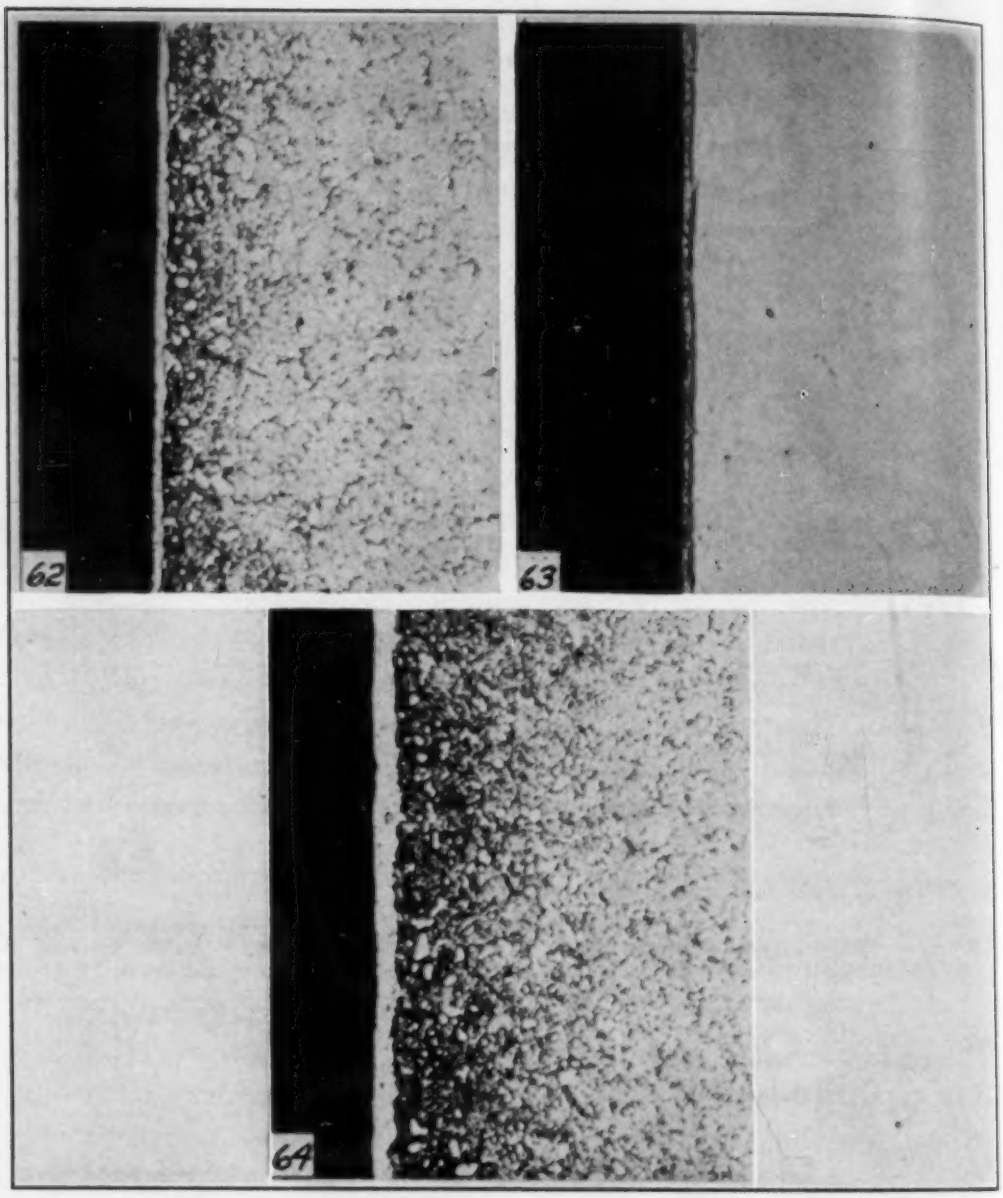


Fig. 62—Sample No. 46. Same as Sample No. 40 Except Plated with Nickel to 0.0001 Inch Thickness Before Nitriding. Etchant 4 Per Cent Nital. × 500.
Fig. 63—Sample No. 46. Unetched. × 500.
Fig. 64—Sample No. 47. Same as Sample No. 40 Except Plated with Nickel to 0.0002 Inch Thickness Before Nitriding. Etchant 4 Per Cent Nital. × 500.

The samples were trued by grinding all surfaces and an additional 0.003 inch removed to a good smooth finish. All the samples were then scrubbed on all surfaces with fine emery and oil to remove "whiskers" and surface "hair" resulting from grinding, after which they were washed in benzol several times, dried and weighed. The samples were then nitrided at various temperatures for various periods of time. The samples were not preheated prior to immersion.

After nitriding, the samples were cooled in natural air, washed to remove adherent salt and then scrubbed on all surfaces with emery and oil to remove surface smudge. The samples were then washed in benzol, dried and weighed. The differences in weights represented the change in weight due to nitriding. A number of the samples were then placed in cold 25 per cent nitric acid for about 20 minutes. The surface of each sample was rubbed with a rubber policeman and washed with distilled water. The samples were again dried and weighed. The difference in weight represented the weight of the analytical sample. Table XXI gives the results of the changes in weight of the rectangular and the round samples due to nitriding at various temperatures for various periods. Table XXII gives the results of the nickel analyses of the stripped surfaces of the nitrided samples.

Examination of Table XXII reveals an erratic pattern as regards the deposition of nickel from the bath on to the surface of the immersed samples. Sample 34R nitrided for 92 minutes shows practically no nickel added to the surface, whereas sample 33R nitrided for 32 minutes shows a considerable amount of nickel to have plated onto the surface. These samples were immersed at the same time, the only apparent variable being the time of immersion. Cylindrical sample 39C was nitrided to check rectangular sample 31R. Even though the surface area of the cylindrical sample is smaller, the amount of nickel deposited is 2½ times that deposited on the rectangular sample. Cylindrical sample 40C was run to check rectangular sample 34R. Again there was a considerable disparity in the amount of nickel deposited. Practically no nickel was added to sample 34R, whereas sample 40C indicated a considerable plate.

The efficiency of a nickel plated surface as a preventive to the absorption of nitrogen during the nitriding of the nitralloy steels by dissociated ammonia is well known. It was felt that high speed steel nitrided in a bath contaminated with nickel which plated onto the surface of immersed parts would also tend to act as a deterrent to the absorption of nitrogen.

Fused cyanides are excellent electrolytes. Consequently, an investigation of nitrided samples electrically insulated was carried out to determine if this would prevent the deposition of nickel. Samples were electrically insulated by placing them in iron wire saddles and suspending them from glass rods, care being taken to prevent any contact with the pot or furnace.

It was found that the nickel deposited on the electrically insulated samples as well as on the noninsulating samples. Several treated and ground samples approximately 1x3/8x2 inches were electrically insulated and nitrided for 30 minutes and 2 hours at 1050 degrees Fahr. in a bath containing 0.0085 per cent nickel. The samples measured for thickness of the nickel plate after nitriding showed the following:

Sample nitrided 30 minutes—thickness of nickel plate—0.00002 inch
Sample nitrided 2 hours—thickness of nickel plate—0.00006 inch

A number of treated high speed steel samples 1/32x1x2 inches were then nickel plated to various thicknesses of plate. Four of these samples were nitrided at 1050 degrees Fahr. for 2 hours in a bath containing about 0.002 per cent nickel. A pressed steel pot and a nickel thermocouple protection tube were being used. An inspection of the nickel plate after nitriding showed some erosion of the plate. It is possible little erosion might have taken place had the bath contained the saturation amount of nickel, viz.: 0.0085 per cent. The samples were nicked in half and the cross sections of cases etched in 4 per cent nital and examined under the microscope for depth of case. Below are given the results of this examination:

Sample Number	Thickness of Nickel Plate Inch	Microscopic Depth of Case at ×500—Etched 4% Nital Inch
40	0.00002	0.002
41	0.00003	0.002
46	0.0001	0.0005
47	0.0002	0.0008

It is evident that a nickel plate while not preventing the absorption of nitrogen does slow up the penetration considerably. At a shorter period of immersion the effect of the nickel plate would probably interfere in still greater proportion than that resulting from the 2-hour immersion. Micrographs of the nickel plated and nitrided samples taken at ×500 are shown in Figs. 60 to 64.

The sludge cake obtained by scooping the sludge from the bottom of a nickel-free bath at 1050 degrees Fahr. by means of a perforated scoop or ladle was dissolved in distilled water and washed twenty times by decantation using about 150 cubic centimeters of water each time. The fine sediment first washing onto the filter paper (sample No. 200) and the balance of residue (sample No.

202) were analyzed for chromium, vanadium and nitrogen. Washed sample No. 200 was quite black in color while sample No. 202 was a dark gray, but after drying at 220 degrees Fahr. both samples were brown in color.

	Sample No. 200 (Fine Part of Residue) Per Cent	Sample No. 202 (Coarse Part of Residue) Per Cent
Carbon	....	5.11
Chromium	4.76	1.08
Vanadium	.08	.00
Nitrogen	....	1.31

Several hundred hardened high speed steel test samples were ground all over and then nitrided at 1050 degrees Fahr. for 30 minutes without preheating. Samples after cooling to room temperature were placed in distilled water until the adherent salt dissolved. The samples were then brushed with a clean steel brush to remove the brownish-black surface deposit. After filtering and washing with distilled water to the absence of chlorides and (CN) the residue (sample No. 203) was dried and analyzed with the following results:

Sample No. 203	Per Cent
Chromium	2.93
Vanadium	.34
Nitrogen	.83

When hardened and ground high speed steel is first withdrawn from a nitriding bath (free of nickel) the surfaces show a wet steely metallic lustre. Shortly after removal the surface (containing the adherent salt) comes to a yellowish color which changes as the room temperature is approached to a yellowish-green color with areas showing the characteristic reddish-brown color of Fe_2O_3.

The analysis of the sludge shows a high percentage of carbon and chromium present with only a trace of vanadium. This is consistent with the known fact that the major portion of the chromium is found in the matrix of high speed steel.

This paper has been titled as an introductory study as there remain a number of phases that have not been discussed, one of the most important of which is the compound that is formed by the nitrogen to cause the great increase in surface hardness. The study is being continued and it is hoped that additional information will be obtained which can be made the subject of a future paper.

Summary

1. The melting point of the bath is lowered after the bath has been used and it is possible to maintain the desirable amount of cyanate by making additions of 70 per cent sodium cyanide and 30 per cent potassium cyanide.

2. A freshly prepared bath will contain about 45 per cent of cyanogen while an aged bath will contain only about 24 per cent cyanogen.

3. There are two zones of chemical activity within the bath, one at the surface where it is exposed to the air and the other where contact is made with the surface of the high speed steel.

4. If the bath is contained in a nickel alloy pot or if a nickel protection tube is used for the thermocouple the bath will quickly become contaminated with nickel.

5. When the bath is contaminated with nickel the nickel will plate onto the surface of the work and greatly affect the results. Consequently, a nickel-free bath is preferable.

6. The elimination of nickel from the nitriding bath produces a superior surface and even the appearance of the surface is changed from a dull gray to a metallic lustre.

7. When the work that is immersed in the bath is not electrically insulated there is a galvanic action, the effects of which are distinctly noticeable.

8. Nitrogen determinations indicate that with 30-minute periods of immersion in an aged bath between the temperature of 850 and 1150 degrees Fahr. the major portion of the nitrogen is within the first 0.001 inch of the surface.

9. The brittleness of the surface of high speed steel that has been nitrided in a freshly prepared bath is apparently due to the steepness of the nitrogen gradient rather than to the amount of nitrogen that is present. When the material is held a considerable period of time in a freshly prepared bath the nitrogen diffuses deeper and the gradient is not so sharp and the surface is not unusually brittle.

10. The process should never be used when the surface is decarburized, because of the brittleness that results. Slight softening of the surface from grinding prior to nitriding is not detrimental.

11. Reheating of the steel after nitriding within certain ranges will result in a considerable diffusion of the nitrogen.

12. There appears to be no material difference in the amount of nitrogen that is absorbed between a piece of hardened high speed steel and a piece of annealed high speed steel.

13. Under certain conditions the surface of the steel will have a sooty appearance and it may appear that there has been carbon absorption. The carbon content, however, is confined to the surface but may be entrapped near the surface by a nickel deposit, if the bath is nickel contaminated. Underneath this surface there does not appear to be a carbon absorption as the result of nitriding.

14. It has been found possible to adapt the Knoop method of hardness testing to obtain the surface hardness of nitrided high speed steel. A surface hardness equivalent of over 1100 Brinell appears possible by properly nitriding fully hardened high speed steel.

15. Microscopic examination of the nitrided area does not reveal the presence of any unusual constituent. The nitrided area is darkened more rapidly than the nonnitrided areas when etched with 4 per cent nital. On some specimens observed there was a dull gray area that would indicate further microscopic examination was justifiable.

16. By careful observation of the surface of the material which had been nitrided it might be possible to make deductions as to whether or not the process is operating properly.

Acknowledgments

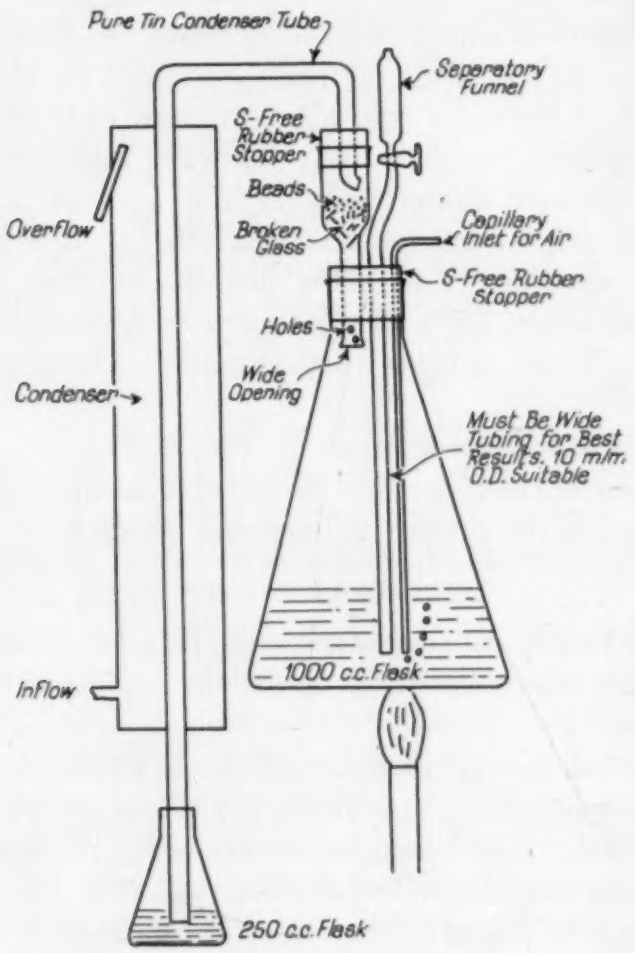
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The generous counsel of Dr. D. A. Holt, Manager of Research, R. & H. Chemicals Division of the E. I. DuPont de Nemours & Co., was most helpful. The DuPont Co. conducted the numerous complete analyses of the salts and of the various baths; Dr. C. G. Peters and Mr. Frederick Knoop of the Bureau of Standards did the work of hardness testing by the Knoop Indenter; Mr. Harry Johnstin of the Metallurgical Department of the Vanadium-Alloys Steel Co. prepared the major portion of the micrographs; Mr. Myron Frost, Chief Chemist of the Vanadium-Alloys Steel Co., conducted the several analyses of the sludge and surface deposits; The Battelle Memorial Institute made the nitrogen determinations; Mr. Wallace Kubacki, Engineer of The Landis Machine Co., made the mathematical analysis of the nitrogen gradient.

Appendix

Method of Analysis for Determining Nitrogen in Steel

Dissolve 5 grams of clean drillings in 50 cubic centimeters of HCl (1.11 sp. gr.) in a 150-cubic centimeter beaker with gentle heat. Invert a larger beaker over the dissolving beaker to prevent



Apparatus for the Determination of Nitrogen in Steel.

contamination. While the sample is dissolving, place in a 1000-cubic centimeter flask (see diagram) 500 cubic centimeters distilled water, 40 grams sodium potassium tartrate, and 40 cubic centimeters sodium hydroxide solution. Light the flame under the flask and commence distilling off water. The air comes from the compressed air line

and is purified as it passes through a soda-lime tube and a bottle of 1:4 H_2SO_4. It is well to follow the H_2SO_4 bottle with a tube of glass wool to remove any possible acid spray that might be present. The air takes the place of hydrogen supplied by mossy zinc—a source of gas often employed in nitrogen determinations. We have tried both and prefer the air method. If it becomes desirable, the rate of flow of air may be increased. The trap shown in the diagram has a few pieces of thin sheet glass in the bottom to prevent the beads above from falling through. It is also desirable to have a few large beads present. A pasteboard or asbestos jacket around the trap aids in preventing moisture from collecting there.

No definite amount of water is distilled over before the introduction of the sample, but distillation is continued until about 25 cubic centimeters of the distillate no longer gives any purple tint with brom cresol purple. Usually 200 to 300 cubic centimeters of distilled water suffices.

The flame is now turned down a trifle and the iron solution is introduced into the bulb of the separatory funnel, the stopcock being closed. A 250-cubic centimeter Erlenmeyer flask containing 10 cubic centimeters of 0.01 N. H_2SO_4 is used as the receiver, the liquid in the flask closing off the tip of the condenser. Samples high in nitrogen may require more than 10 cubic centimeters of standard acid. A little water may be added, if necessary, to close off the tip of the condenser. The flame under the flask should be sufficient to prevent the liquid from sucking back. The pressure of the air through the capillary makes it possible to add the iron solution somewhat more rapidly than when mossy zinc is employed. The tartarate produces a semi-colloidal solution that tends to prevent lumping. The iron solution is run in slowly in successive small portions, the contents of the flask being allowed to boil gently for a few minutes after each addition. One must be careful not to boil the solution too vigorously.

After all the iron solution has been added, 150 cubic centimeters of distilled water is added through the separatory funnel in small portions. We have made the following test:

After the system was free of volatile alkaline substances a 50-cubic centimeter portion of distilled water was introduced through the separatory funnel and 50 cubic centimeters of distillate caught. The distillate when titrated in the presence of brom cresol purple indicator showed no ammoniacal substances. This shows that spe-

cial "ammonia-free" distilled water is not essential. At least it is not essential in the case of *our* distilled water.

About 200 cubic centimeters of distillate is caught. This is transferred to a 750-cubic centimeter Erlenmeyer flask and CO_2-free air is drawn, by means of a suction pump, through the solution for 10 to 15 minutes. (CO_2-free air made by drawing the air through a 30-inch column of soda lime.) Without shutting off the suction pump 4 drops of brom cresol purple are introduced and 0.01 N NaOH added from a burette until a greenish-pink color is obtained. One more drop should give a pale violet. It is well to use a 3-hole stopper, permitting the tip of the burette to pass through one of the holes. In this way the CO_2-free air may be sucked through the solution during titration.

A blank is carried through in the same manner as the determination, except that HCl has no steel dissolved in it. In calculating the nitrogen in a sample the number of cubic centimeters of 0.01 N NaOH required to titrate the excess H_2SO_4 is subtracted from the number required in the blank and the difference is multiplied by the N factor of the standard NaOH.

Solutions Required:

Hydrochloric Acid. A freshly opened bottle is used in preparing a reagent of sp. gr. 1.11 (hydrometer).

Sodium Hydroxide. 600 grams of pure stick NaOH is dissolved in 1 liter of water and digested on a Zn-Cu couple at 120 degrees Fahr. for 48 hours. The liquid is then decanted and filtered into a clean flask, boiled for a few minutes to remove any ammonia, and sealed with a paraffined cork. The Zn-Cu couple is prepared by treating 50 grams of sheet zinc with a warm solution of $CuSO_4$ for 10 minutes. The copper solution is decanted and the zinc, covered with spongy copper, is washed several times with distilled water.

0.01 N. H_2SO_4. Add 0.28 cubic centimeter concentrated H_2SO_4 per liter of water and check strength against 0.01 N NaOH.

0.01 N NaOH. Make 0.1 N NaOH and standardize against Bureau of Standards' potassium-acid phthalate. Dilute to make 0.01 N.

Brom Cresol Purple. 0.4 per cent aqueous solution.

The necks of bottles containing reagents for nitrogen determination should be protected from ammonium chloride in the laboratory by having beakers turned down over them.

Method of Determining the Nitrogen Content of Successive One Ten-Thousandths Inch of Sample

For the determination of the nitrogen content of successive one ten-thousandths inch of surface, the data of Table VII is used. Hereafter, for convenience, samples N25, N21, N22, N23, and N24 will be referred to as Samples No. 1, No. 2, No. 3, No. 4, and No. 5, respectively. The data of Tables IV and V also have been utilized, in that the values of 0.02 per cent nitrogen and 0.01 per cent nitrogen for the nitrogen contents of the layers 0.001 to 0.002 inch and 0.002 to 0.003 inch, respectively, have been taken therefrom.

Determination of the nitrogen content of First one ten-thousandth Inch:

For the determination of the nitrogen content of the first one ten-thousandth of an inch, only the data concerning Samples No. 1 and No. 2 can be considered. This follows because Sample No. 1 is the only one which contains the first one ten-thousandth, while Sample No. 2 is the only one which contains all the remainder of the first thousandth of metal whose nitrogen content is unknown. It will later be obvious that this is an unfortunate situation, for the data on Sample No. 2 appear erroneous. However, the computed value of 1.105 per cent nitrogen is at least indicative of the high nitrogen content of the first one ten-thousandth inch.

Throughout this and all subsequent determinations it will be assumed that the weight of sample for each one ten-thousandth of cut will be the same. Since the original diameter of the samples is approximately 1.7150 inches, the error introduced by this assumption is of small importance.

From Sample No. 1 were cut 0.0023-0.0000 inch or 23 parts whose average nitrogen content was 0.104 per cent.

From Sample No. 2 were cut 0.0021-0.0001 inch or 20 parts whose average nitrogen content was 0.063 per cent.

Thus, the elimination of the first plus the twenty-second and twenty-third one ten-thousandths has resulted in decreasing the average nitrogen content of Sample No. 2. Since most of this decrease has resulted from the elimination of the first one ten-thousandth, the nitrogen content thereof can be found.

Let X = per cent of nitrogen in first ten-thousandth;
and Y = per cent of nitrogen in second to tenth ten-thousandths, inclusive.

Then,

(1) $0.104\%\ N \times 23 \text{ parts} =$
$X\%\ N \times 1 \text{ part} + Y\%\ N \times 9 \text{ parts} + 0.020\%\ N \times 10 \text{ parts} + 0.015\%\ N \times 3 \text{ parts}$

Or in other words, the nitrogen content of Sample No. 1 is equal to the sum of the nitrogen contents of the first one ten-thousandth inch plus that of the next nine ten-thousandths inches plus that of the next ten ten-thousandths inches plus that of the next three ten-thousandths inches.

It should be noted that the average nitrogen content of the range ten to twenty ten-thousandth inches is assumed to be 0.020 per cent and that of the range twenty to thirty ten-thousandth inches is assumed to be 0.010 per cent. A straight line gradient is assumed there between to give the values listed above.

In similar fashion, from Sample No. 2 we have,

$0.063\%\ N \times 20 \text{ parts} =$
$Y\%\ N \times 9 \text{ parts} + 0.020\%\ N \times 10 \text{ parts} + 0.015\%\ N \times 1 \text{ part}$

Solving for 9Y, we obtain the value 1.045 which is immediately placed in (1) to yield a value of 1.105 per cent N for X, the percentage of nitrogen in the first ten-thousandth inch of Sample No. 1.

Determination of the nitrogen content of Second one ten-thousandth Inch:

From Sample No. 2 were cut 0.0021-0.0001 inch or 20 parts whose average nitrogen content was 0.063 per cent.

From Sample No. 3 were cut 0.0022-0.0002 inch or 20 parts whose average nitrogen content was 0.067 per cent.

Thus, the substitution of the twenty-second one ten-thousandth for the second one ten-thousandth resulted in having a higher average nitrogen content in Sample No. 3. This obviously is in error; however, the determination of the nitrogen content of the second one ten-thousandth is herein listed merely to show the manner in which it would be computed.

Let W = per cent of nitrogen in second ten-thousandth;
and V = per cent of nitrogen in third to tenth ten-thousandths, inclusive.

Then,

(2) $0.063\%\ N \times 20 \text{ parts} =$
$W\% \times 1 \text{ part} + V\% \times 8 \text{ parts} + 0.020\% \times 10 \text{ parts} + 0.015\% \times 1 \text{ part}$

and

(3) 0.067% N × 20 parts =
V% × 8 parts + 0.020% N × 10 parts + 0.014% N × 2 parts

Note: It should be noted that the nitrogen content values for the range twenty to thirty ten-thousandths are computed by interpolation as explained previously.

Now, solving for 8V from (3), we have 8V = 1.112

Substituting this value in (2), we have W = —0.067 per cent nitrogen, or the nitrogen content of the second ten-thousandth is —0.067 per cent.

While this value is perfectly possible from an algebraic viewpoint, it appears absurd. Naturally, either the experimental value of the nitrogen content of Sample No. 2 is too low, or that of Sample No. 3 is too high. It later will be seen that the former is very probably correct.

Determination of the nitrogen content of Third one ten-thousandth Inch:

From Sample No. 3 were cut 0.0022-0.0002 inch or 20 parts whose average nitrogen content was 0.067 per cent.

From Sample No. 4 were cut 0.0023-0.0003 inch or 20 parts whose average nitrogen content was 0.056 per cent.

Thus, the substitution of the twenty-third one ten-thousandth for the third one ten-thousandth resulted in having a lower average nitrogen content in Sample No. 4. This, naturally, is what was to be expected. The manner of computing the nitrogen content of the third one ten-thousandth inch is parallel to that employed in obtaining the value of that of the second one ten-thousandth inch; therefore, only the equations employed are listed below.

Let T = per cent of nitrogen in third ten-thousandth;
and S = per cent of nitrogen in fourth to tenth ten-thousandths, inclusive.

Then,

0.067% N × 20 parts =
T% Y × 1 part + S% N × 7 parts + 0.020% N × 10 parts + 0.014% N × 2 parts

and

0.056% N × 20 parts
S% N × 7 parts + 0.020% N × 10 parts + 0.014% × 3 parts

Since 7S is computed to be 0.878 from (4'), T, the nitrogen content of the third ten-thousandth is computed to be 0.236 per cent, from substituting value of 7S in (3).

This value of 0.236 per cent nitrogen can be accepted with some degree of plausibility.

Determination of nitrogen content of Fourth one ten-thousandth Inch:

From Sample No. 4 were cut 0.0023-0.0003 inch or 20 parts whose average nitrogen content was 0.056 per cent.

From Sample No. 5 were cut 0.0029-0.0004 inch or 25 parts whose average nitrogen content was 0.043 per cent.

Thus, in effect, the substitution of the twenty-fourth one ten-thousandth for the fourth one ten-thousandth (since the nitrogen content of the twenty-fifth to the twenty-ninth ten-thousandths can be found by interpolation, it does not really influence the experimental value from a computation viewpoint even though it must be considered) resulted in having a lower average nitrogen content in Sample No. 5. This, again, was to be expected.

Now, let R = per cent nitrogen in fourth one ten-thousandth;
and S = per cent nitrogen in fifth to tenth one ten-thousandths, inclusive.

Then,

(4) $0.056\%\ N \times 20 \text{ parts} =$
$R\%\ N \times 1 \text{ part} + S\%\ N \times 6 \text{ parts} + 0.020\%\ N \times 10 \text{ parts} + 0.014\%\ N \times 3 \text{ parts}$

and

(5) $0.043\%\ N \times 25 \text{ parts} =$
$S\%\ N \times 6 \text{ parts} + 0.020\%\ N \times 10 \text{ parts} + 0.011\%\ N \times 9 \text{ parts}$

From (5) the value of 6S is computed to be 0.N6.

This results in yielding a value of 0.102% N for R (from (4) by substituting 0.776 for 6S)

Thus, the fourth one ten-thousandth has a computed nitrogen content of 0.102 per cent.

Optional Method of Determining Nitrogen Content of Second one ten-thousandth Inch:

Since it is known that the nitrogen content computed for Sample No. 2 is erroneous, the nitrogen content thereof can optionally be computed by finding the nitrogen content of the combined first and second one ten-thousandths and then subtracting that of the first

one ten-thousandth therefrom to yield the nitrogen content of the second one ten-thousandth.

For this purpose, the data concerning Samples No. 1 and No. 3 are used.

Now, let P = per cent nitrogen in first and second one ten-thousandths;

and Θ = per cent nitrogen in third to tenth one ten-thousandths, inclusive.

Then, from Sample No. 1,

$$0.104\% \text{ N} \times 23 \text{ parts} =$$
$$\text{P}\% \text{ N} \times 2 \text{ parts} + \Theta\% \text{ N} \times 8 \text{ parts} + 0.020\% \text{ N} \times 10 \text{ parts} + 0.014\% \text{ N} \times 3 \text{ parts}$$

and from Sample No. 3,

$$0.067\% \text{ N} \times 20 \text{ parts} =$$
$$\Theta\% \text{ N} \times 8 \text{ parts} + 0.020\% \text{ N} \times 10 \text{ parts} + 0.014\% \text{ N} \times 2 \text{ parts}$$

This yields a value of 1.112 for 8Θ and one of 1.028 for P, which further gives 0.514 per cent for P, the average nitrogen content of the first and second one ten-thousandths.

However, since the first one ten-thousandth, alone, has sufficient nitrogen to yield a nitrogen content of $1.105\% \div 2$ or 0.553 per cent nitrogen for these two ten-thousandths even if the second one ten-thousandth had no nitrogen, it is obvious that the second one ten-thousandth must have a negative nitrogen content to yield the computed value of 0.514 per cent average nitrogen content for the first two ten-thousandths. This negative nitrogen content is computed to be 1.028-1.105 or —0.077 per cent nitrogen or perhaps more clearly 2(0.514%-0.553%) which yields, again, —0.077 per cent nitrogen.

Further Optional Method of Determining Nitrogen Content of Second one ten-thousandth Inch:

In similar fashion to the computation just made, the nitrogen content of the second one ten-thousandth can be determined by computing that of the first three ten-thousandths and substituting therefrom the already computed values of the nitrogen content of the first and that of the third one ten-thousandth to yield the nitrogen content of the second one ten-thousandth.

For this purpose, the data concerning Samples No. 1 and No. 4 are used.

Now, let N = per cent nitrogen in first three ten-thousandths;

and M = per cent nitrogen in fourth to tenth one ten-thousandths,

Then, for Sample No. 1,

0.104% N × 23 parts =

N% N × 3 parts + M% N × 7 parts + 0.020% N × 10 parts + 0.014% N × 3 parts

and from Sample No. 4,

0.053% N × 20 parts =

M% N × 7 parts + 0.020% N × 10 parts + 0.014% N × 2 parts

This yields a value of 1.332 for 7M and one of 1.332 for 3N, which further gives 0.444 per cent for nitrogen, the average nitrogen content of the first, one three ten-thousandths.

Now, the first one ten-thousandth, alone, has a nitrogen content of 1.105 per cent, and that of the third one ten-thousandth is 0.236 per cent. Combining these two, we have 1.341 as a figure indicative of the actual nitrogen in both of these parts. This compares with a value of 1.332 for the figure indicative of the actual nitrogen in the first three ten-thousandths; thus, the second ten-thousandth inch has a nitrogen content of 1.333-1.341 or —0.009 per cent nitrogen.

Conclusion

1. The computed nitrogen content data for Sample No. 2 shows that the experimental data concerning this run are in error:

(a) Because it yields negative nitrogen content values therefor.

(b) Because it influences the computation for the nitrogen content of the first one ten-thousandth to the extent that the computed value therefor is obviously too high.

2. No sufficient degree of accuracy concerning the nitrogen content value of the second or third thousandth of metal is available, for the assumed values of 0.020 and 0.010 per cent, respectively, are subject to ± 0.001 per cent nitrogen variation due to chemical experimental error.

3. The probable nitrogen content values of each of the four ten-thousandths could be listed as follows if the experimental value for Sample No. 2 had been approximately 0.08 per cent, which value it should approximate to be consistent with the other experimental runs comprising this series:

First one ten-thousandth—0.7-0.8 per cent nitrogen
Second one ten-thousandth—0.35-0.45 per cent nitrogen
Third one ten-thousandth—0.2-0.3 per cent nitrogen
Fourth one ten-thousandth—0.090-0.115 per cent nitrogen.

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DISCUSSION

Written Discussion: By Vincent O. Stromberg, metallurgical engineer, John Bath & Co., Inc., Worcester, Mass.

The paper which introduces study of the nitriding of hardened high speed steel by the use of molten cyanides was found to be most interesting and instructive. The writer was most keenly interested in the discussions which deal with the hardness testing of cyanided cases on hardened high speed steel. The question is frequently asked us as to what the hardness of the surface might be on a hardened and thread ground high speed steel nitrided tap. Of course, a very quick test is to use a file. However, the author tried to satisfy his curiosity by trying to devise a method whereby we could determine the hardness of the case in such a way that we might refer to it in terms of either Rockwell "C" or Brinell numbers.

The method used was not entirely original since the Mechanical Engineering Department of Worcester Polytechnic Institute once used this method to determine hardness of very thin sections of metal. However, the writer found this method to be a help in trying to make a determination of hardness on cyanided surfaces on high speed steel tools. In this method we make use of the Brale or Rockwell diamond penetrator which has a radius of curvature of 0.2 millimeter on the point and has an included angle of 120 degrees on its conical shape. With this penetration a small Brinell indentation is made. The standard Brinell machine has a 10-millimeter ball which is subjected to 3000-kilogram load. The Brale point might be considered to be a 0.4-millimeter "ball" which might be subjected to a lighter load which would be in some proportion to a Brinell tester.

In the Brinell testing, the load on the ball might be considered to be proportional to the square of the diameter.

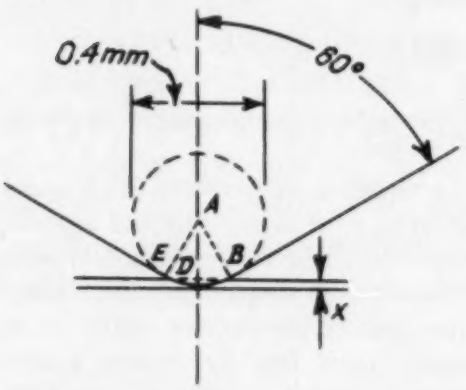
$$\frac{3000\ \text{Kg}}{X\ \text{Kg}} = \left(\frac{10\ \text{m/m}}{0.4\ \text{m/m}}\right)^2$$

$$X = \frac{3000}{\left(\frac{10}{0.4}\right)^2} \quad \text{or} \quad \frac{3000}{(25)^2}$$

$$X = 4.5 \text{ Kg or } 10.584 \text{ pounds}$$

If a load of 4.5 kilograms and a ball of 0.4 millimeter diameter be used, a miniature Brinell machine can be made which is exactly 1/25 size. Therefore, any indentation made with this machine will be 25 times smaller than a standard Brinell Indentation.

Since the Brale is of conical shape and of dimensions shown in the figure, it becomes first necessary to determine the maximum allowable penetration in order to get an accurate reading.



A B = 0.2 millimeters

Angle D A B = 30 degrees

A D = AB (COS 30 degrees)

$$A D = 0.2 \left(\frac{\sqrt{3}}{2}\right) = 0.1732$$

Maximum Depth of Penetration then = 0.2000 — 0.1732, or
0.0268 millimeters or
Since 1 millimeter = 0.0394 inches
Maximum depth in inches = 0.00105 inches.
To determine the diameter of impression
D B = 0.2 (sin 30) or 0.2 (½) = 0.1 radius
or 0.2 millimeter diameter of surface impression.

In terms of a 3000-kilogram load a 10-millimeter ball
0.2 × 25 = 5.0 millimeter impression diameter
5.00 = 143 Brinell.

In assuming that high speed steel tested in this manner is always over 62 Rockwell "C", it can be found that the depth of penetration will be no more than 0.00005 inch.

In studying hardness of nitrided cases, we have assumed a maximum case depth of about 0.001 of an inch. Therefore, this hardness testing device will not allow the point to penetrate the case.

In making the measurements it is quite obvious that the impressions are very small. These impressions are measured under the microscope at a magnification of 250 times. The diameter of the enlarged image is then measured

and the reading obtained is divided by 10. Then the Brinell reading can be obtained from a standard table based on 3000-kilogram load and 10-millimeter ball. Using this method, hardnesses of nitrided surfaces have been found to be 70 to 74 Rockwell "C" in a number of cases. Sometimes the hardness is less or greater depending on the condition of the bath, time, temperature, etc., as has been pointed out in the excellent discussion of Messrs. Morrison and Gill.

Written Discussion: By Edgar K. Spring, metallurgist, Henry Disston & Sons, Inc., Philadelphia.

The portion of this paper dealing with reactions within the bath itself are extremely interesting as pointing definitely to methods of control of nitriding baths. Such control should serve to produce a more stable, dependable process, doing away with at least a part of those unexplained failures of the process experienced at times.

If I read the paper correctly, I believe the writers consider a salt bath for nitriding should be confined to that process only and not diverted to cyaniding. The breakdown of the salt at the higher temperatures is appreciably more rapid. In spite of this, however, such double use of the bath is frequently resorted to and must cause early failure of the bath to properly perform the functions expected.

The physical character of the case probably explains why nitrided cases on annealed high speed steel could be removed by filing. The great hardness of the case carries with it the characteristic of great brittleness. The relatively soft bars (annealed high speed steel) "gave" sufficiently under pressure so that the friable hard case cracked away and came off by spalling, not true filing, which accounts for the necessity of hardening and tempering the steel before applying the nitride case. While the case takes the wear of subsequent service it must be backed up by a sufficiently strong, stiff backing so that the inherent brittleness of the case does not become a cause of failure.

The hardness numbers computed from the Knoop Indenter are about those computed for nitrided cases and published previously. This newer method, however, more surely establishes the order of hardness of nitrided cases confirming the general conception.

It is pointed out on page 980 that the nitriding of decarburized high speed steel and nitralloy should not be undertaken. This obviously applies to deeply decarburized surfaces. Might I ask the authors' opinion of the reasonableness of nitriding where the decarburized depth is of the same order as that of the nitride case applied?

The authors are to be complimented on the thoroughness with which they have covered a method so old as to have had much less attention than its due.

Written Discussion: By G. V. Luerssen, metallurgist, Carpenter Steel Co., Reading, Pa.

This paper contains such a wealth of fresh and valuable information on the cyaniding of high speed steel, and embodies such a thorough survey of the subject, that discussion of the results becomes quite difficult. The authors are to be congratulated on the thoroughness with which they did their job, and particularly the completeness of the presentation of data. In pioneering work such as is represented by this paper, the presentation of as much original data as possible is extremely helpful to subsequent workers in the field.

Under the heading of "Galvanic Characteristics of the Bath" the change in polarity during the first few minutes of heating is quite interesting, and I would like to ask if the authors have considered the possibility that this rapid change might be explained by the actual heating of the specimen. I should like to ask if the authors preheated any specimens to bath temperature before introducing into the cyanide bath, comparing the galvanic behavior of these specimens with those not so preheated. Such procedure would show definitely whether or not the temperature differential between the specimen and the bath has an effect on the electrical potential.

The writers are to be congratulated upon a very comprehensive and valuable contribution to the literature of high speed steel.

Oral Discussion

W. H. WILLS:[1] I merely want to ask a question regarding this paper. Have the authors noticed any connection between the depth of nitrided case and the susceptibility of tools given this treatment to chipping? I have run across instances where if the depth is appreciably over 1/1000 of an inch there is some danger of tools chipping.

Authors' Reply

We appreciate the generous comments made on this paper. In regard to Mr. Wills' question about the possibility of gaging the brittleness of a nitrided case by means of microscopic examination, it is questionable if one could do this with any degree of sureness. Microscopically, there may be some evidence of brittleness but we have not been able to determine what this evidence might be. The character of the areas about the short micro-axis of the impressions made by the Knoop Indenter appears to be some gage of the brittleness of the surface. With increasing brittleness there appears to be an increase in microscopic distortion or cracking.

Regarding Mr. Stromberg's comment in connection with the use of the modified Brinell, it is indeed interesting and may be of value if given further study.

Mr. Spring raises the question of the reasonableness of nitriding where the order of decarburization is of the same depth as that of the nitride case. Decarburization is a rather broad field as it is sometimes a matter of opinion if a surface is decarburized. Decarburization may be total or it may be partial to varying degrees. In the case of a partial decarburization which does not approach too closely that of total decarburization, nitriding would very probably be of value. Nitriding is also of some assistance in order to modify the extremely thin soft film found on the broad areas of hardened high speed steel as distinguished from the surface condition found on outside corners or on sharp projections.

Mr. Luerssen raises the question of the influence of the method of heating on the character of the galvanic curves. Preheating the specimens to the same temperature as that used in nitriding does alter the galvanic patterns in that the specimens are not anodic immediately following immersion. However, there is little alteration to the positive millivoltage patterns.

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THE TEMPERING OF HIGH SPEED STEEL

By Morris Cohen and P. K. Koh

Abstract

The mechanism of tempering and secondary hardening in 18-4-1 high speed steel has been investigated by means of X-ray, hardness, specific volume, electrical resistance, metallographic, dilatometric and magnetic measurements on hardened specimens tempered at several temperatures for times ranging from about one minute to several hundred hours. At some temperatures, single tempering was directly compared with multiple tempering. A detailed picture of the tempering process is presented in which the secondary hardening is attributed to the precipitation of complex carbides from the residual austenite and the transformation of this austenite into martensite. The austenite transforms during the cooling from the tempering temperature, and the amount which transforms depends principally upon the time and temperature of the tempering treatment (hardening conditions being constant). The effects of other variables on the austenite transformation have also been studied.

On the basis of these results, a straightforward explanation is offered to account for the reported differences obtained from multiple tempering as compared with single tempering.

THE tempering of high speed steel represents a vital part of its normal heat treatment because of the phenomenon of secondary hardening. Quenched or hardened high speed steel softens appreciably when tempered in the range generally used for plain carbon and low alloy tool steels, but when the tempering temperature is raised to 1000 or 1100 degrees Fahr. (540, 595 degrees Cent.),

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Part of this paper is based on a thesis submitted by P. K. Koh in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology, February, 1939.

A paper presented before the Twenty-first Annual Convention of the Society held in Chicago, October 23 to 27, 1939. Of the authors, Morris Cohen is assistant professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts, and P. K. Koh is associated with the Patent Shaft and Axletree Company, Wednesbury, England. Manuscript received June 26, 1939.

high speed steel develops a secondary hardness which is of the same order of magnitude as the original quenched hardness. Thus, by tempering hardened high speed steel at 1050 degrees Fahr. (565 degrees Cent.), the quenching stresses may be relieved to a substantial degree without much, if any, sacrifice of hardness. This is to be contrasted with ordinary hardened tool steels which become too soft for tool applications if tempered at this comparatively high temperature.

The mechanism of tempering and secondary hardening in high speed steel has received considerable study both in this country and abroad. Yet, there are many phases of this problem which require clarification. For example: (A) As a result of X-ray (1),[1] density (1), (2), (3), change in length (1), magnetic (3), (4), metallographic (1), (4), (5), and electrical resistance (3) studies on the tempering of high speed steel, it is now commonly believed that the secondary hardening results from the transformation of residual austenite which has been retained by the quench of the previous hardening operation. Grossmann and Bain (1) have correlated most of this work and have presented the arguments supporting this mechanism of secondary hardening. Unfortunately, the X-ray technique, which in general is capable of yielding the most positive evidence of a crystal lattice transformation, becomes quite involved when applied to high speed steel because of the large number of alloy carbide lines appearing in the X-ray photograms. The pioneering work of Grossmann and Bain (1) in this direction demonstrated that austenite is certainly retained in quenched high speed steel, and that this austenite transforms after tempering at 1300 degrees Fahr. (705 degrees Cent.), but no connection was shown between the transformation and the secondary hardening by this method. The magnetic changes which occur during the tempering of high speed steel have been accepted by many investigators as direct evidence of the austenite transformation, and while this assumption seems justified, reference should be made to the work of Zavarine (7) and Smith (6) who found that the change from the paramagnetic to the ferromagnetic state in steel does not necessarily coincide with the austenite-to-ferrite lattice transformation. The results of the other types of measurements mentioned above are all consistent with the austenite transformation hypothesis, but cannot be considered as conclusive proof. In fact, Houdremont, Bennek,

[1] The figures appearing in parentheses refer to the bibliography appended to this paper.

and Schrader (8) have attributed the secondary hardening of high speed steel, at least in part, to the precipitation of alloy carbides from a supersaturated matrix. Further X-ray studies seem necessary for a positive determination of the cause of secondary hardening.

(B) Very little information is available on the effect of the time of tempering. Most of the work on the secondary hardening of high speed steel has been confined to tempering times of one half to two hours, and the measured properties are usually plotted against temperature rather than time. This method of investigation may not be sufficiently intensive to detect easily-obscured processes in the tempering mechanism, such as are revealed in age-hardening studies by conducting measurements over prolonged periods of time at several temperatures (9).

(C) Several papers (10-14) have appeared in foreign journals which offer magnetic and dilatometric evidence that the residual austenite in hardened high speed steel does not transform at the tempering temperature but rather during the cooling from this temperature. It is surprising to note that this work has received little attention in this country. Our own literature is meagre on this phase of the subject, and further investigation is warranted.

(D) A question exists as to the relative merits of single and multiple tempering of high speed steel. Reports have been received that tempering high speed steel two or three times produces longer tool life and greater permanency of dimensions after final grinding than when the steel is tempered once for an equivalent length of time. This longer tool life has been ascribed variously to greater "toughness", higher "fatigue resistance" and lower "notch sensitivity". The quotation marks are used advisedly since these remarks are based on the personal impressions (rather than experimental determinations) of several users of high speed steel. The authors are not aware of any investigation which has been designed to establish fundamentally the possible difference between single and multiple tempering of high speed steel.

The present paper represents the results of a 2-year investigation on the tempering of 18-4-1 high speed steel by means of Rockwell C hardness, X-ray, specific volume, electrical resistance, microscopic, dilatometric and magnetic measurements. Based on these studies, a detailed picture of the tempering mechanism in high speed steel is offered which, in turn, seems to clarify the controversial points enumerated above.

Experimental Details

Types of Measurement—The high speed steel used for this investigation was obtained from regular commercial stock through the courtesy of Mr. James P. Gill of the Vanadium-Alloys Steel Company. The steel was received as annealed in the following three forms as shown in Table I. It is evident that these three steels fall within the usual classification of 18-4-1 high speed steel.

Table I
Composition and Form of High Speed Steel Studied

Heat No.	Size of Stock	C	Mn	S	P	Si	W	Cr	V	Surface Condition
6854	½" square	0.72	0.23	Tr.	0.016	0.36	17.84	3.92	0.98	Oxidized
6852	¼" round	0.735	0.22	Tr.	0.018	0.32	17.84	3.98	1.17	Slightly Oxidized
5988	$\frac{1}{16}$" round	0.71	0.24	Tr.	0.016	0.28	18.01	4.11	1.02	Bright

The oxidized surface of the ½-inch square and the ¼-inch round stock was completely removed by grinding in order to pre-

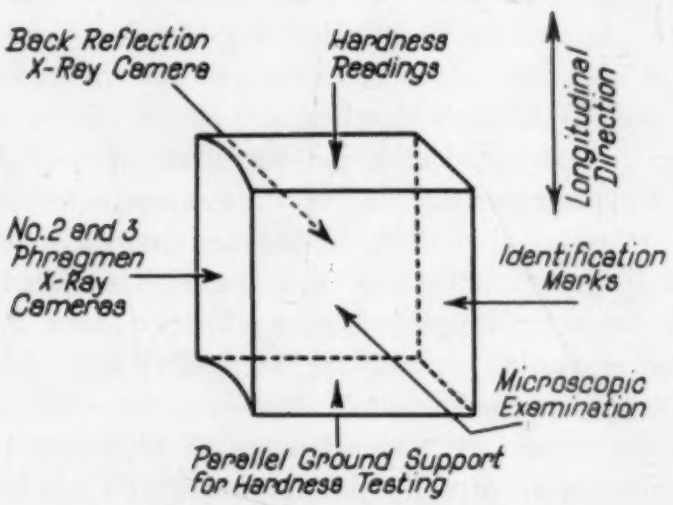


Fig. 1—Shape of Specimens Used for the X-ray, Metallographic, Hardness and Specific Volume Measurements.

vent possible decarburization by the oxide during the subsequent heat treatment. The ½-inch square bar was then cut into ½-inch lengths, and one longitudinal surface of each cube was cylindrically ground (concave) to approximate the curvature of a Phragmen X-ray camera. As shown in Fig. 1, these specimens were used for X-ray studies on three cameras, for microscopic examination, and

for hardness as well as specific volume determinations. The term specific volume, rather than its reciprocal, the density, will be used throughout this discussion because it can be correlated more readily with the dilatometric data.

The X-ray pictures were taken on a No. 2 (intermediate range) Phragmen camera (15), a No. 3 (outer range) Phragmen camera (15), and a back-reflection (precision) camera (16) using chromium radiation from a modified Hägg X-ray tube (16). The No. 2 Phragmen photograms were used for checking the crystal structure of the carbides, for measuring the positions and intensities of the residual austenite lines, and for examining the quality of the martensite or ferrite lines. The No. 3 Phragmen photograms supplied additional lines for checking the structure of the carbides, but these lines obscured those of the austenite. The back-reflection photograms were used to determine the lattice parameters of the ferrite and carbides. No austenite lines appeared in the back-reflection pictures, and hence the lattice parameters of the residual austenite had to be determined from the less precise No. 2 Phragmen photograms. However, the carbide lines were quite sharp. and their positions did not change as a result of hardening and tempering. By measuring the positions of the austenite lines with reference to a certain intense carbide line (whose position was accurately known from the lattice parameter measurements made with the back-reflection camera), the austenite lattice parameters could be measured to $\pm$ 0.003 A.U. The relative intensities of the austenite lines were determined at critical stages of tempering at 1050 degrees Fahr. with a recording microphotometer. Except for the annealed high speed steel, the ferrite lines were quite broad even though the specimens were deeply etched to relieve surface strains. For this reason the ferrite parameters have been plotted as a range of values corresponding to the width of the unresolved $K\alpha$ (2 1 1) line in the back-reflection photograms.

The hardness readings were made with a new Rockwell hardness tester. The machine was checked with a standard hardness block before each set of readings. At least five, and sometimes ten, readings were taken at each tempering interval. It is believed that the results are accurate to $\pm$ ½ unit on the Rockwell C scale.

The specific volume determinations were made by the well known method of weighing in air and in distilled water. By reducing the surface tension of the water with a trace of a wetting re-

agent,[2] and by carefully cleaning the specimens, the specific volume of any given specimen could be checked to ± 1 part in 100,000. However, since the annealed stock varied by ± 2 parts in 10,000 from sample to sample, the latter range is taken as the experimental error in this work. All of the specific volume results have been referred to a room temperature of 72 degrees Fahr. after making the usual corrections for the suspension wire and the density of the water.

The dilation measurements were made on a ¼-inch round stock with a dilatometer described by the American Society for Testing Materials (17). The dial gage, which directly indicated the changes in length of a 4-inch specimen, could be read to ± $\frac{1}{10}$ of a division or ± 0.00001 inch. Seven critical runs were repeated on a Leitz recording dilatometer, and the results were in excellent agreement.

The electrical resistance determinations were carried out at 77 degrees Fahr. on 3-inch lengths of the $\frac{1}{16}$-inch diameter stock, using a Kelvin bridge having an accuracy of ± 0.1 per cent. However, since consecutive 3-inch lengths of the annealed steel varied by as much as ± 1.0 per cent, the changes in resistance during tempering have been plotted to the nearest per cent.

Magnetization versus temperature measurements were made on ½-inch lengths of the $\frac{1}{16}$-inch stock to determine the possible existence of a cementite Curie point[3] in the annealed and heat treated steel. Additional runs were made on the ¼-inch stock to substantiate some of the dilatometer results. The apparatus used has been described in detail by Buehl and Wulff (18). It consisted essentially of a torsion balance arranged to measure the force exerted on a small specimen which was suspended in a furnace in a magnetic field of uniform gradient.

Heat Treatment and Preliminary Tests—The high speed steel specimens were hardened by oil quenching from 2350 ± 10 degrees Fahr. (1290 degrees Cent.). No preheat was used because of the small size and simple shape of the specimens. The high heat treatment was carried out in a globar furnace provided with a carbonaceous muffle. This nonoxidizing atmosphere was used in order to permit longer soaks, and hence to obtain a more uniform

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[2]"Sorbitol Laurate" furnished by the Atlas Powder Company gave excellent results.

[3]These magnetic measurements were made by Mr. A. M. White and were submitted in the form of a Bachelor's thesis at the Massachusetts Institute of Technology.

solution of the carbides than was possible in an oxidizing atmosphere. A superficial carbon pick-up was noted on the specimens, but this was carefully removed with emery paper before proceeding with the tempering tests.

The ½-inch cube specimens were heated for 12 minutes in the high heat furnace prior to the oil quench. A uniform grain size was produced, and most of the specimens had Rockwell C readings of 65.8 to 66.4 and specific volumes of 0.11546 to 0.11551 c.c./gm. The few specimens which had values outside of this range were discarded. The ¼-inch and $\frac{1}{16}$-inch specimens were heated for 6 and 5 minutes respectively in the high heat furnace since these treatments produced the same grain size as was obtained in the ½-inch specimens.

Specimens thus hardened were tempered for lengths of time ranging from about one minute to several hundred hours at temperatures of 212 and 350 degrees Fahr. (100 and 175 degrees Cent.) in oil, at 550, 750 and 900 degrees Fahr. (290, 400 and 480 degrees Cent.) in molten salt, and at temperatures of 1000, 1050 and 1150 degrees Fahr. (540, 565 and 620 degrees Cent.) in molten lead. These tempering temperatures were controlled to ± 5 degrees Fahr. Liquid baths were used for the tempering in order to bring the specimens up to temperature rapidly, and hence to enable an accurate determination of the tempering time.

Except for the dilation and magnetic measurements, which were made at the tempering temperatures, the rest of the measurements were carried out at room temperature. For each tempering temperature, a series of specimens was used, each specimen being tempered for a different length of time. This will be referred to as single tempering in this paper, since each specimen was tempered only once. In addition, multiple or intermittent tempering was carried out at 550, 1050 and 1150 degrees Fahr. (290, 565 and 620 degrees Cent.); that is, the tempering treatments of the specimens were interrupted at periodic intervals, by cooling the specimens to room temperature for the measurements, and then they were returned to the tempering baths until time for the next measurements.

The influence of the rate of cooling following the tempering was given careful consideration since it was necessary to cool rapidly in order to make an accurate determination of the tempering time, and yet it was important to avoid extraneous effects due to cooling stresses. To investigate this variable, three hardened ½-

inch cube specimens were tempered at 1000 degrees Fahr. (540 degrees Cent.), and the tempering was interrupted at certain intervals for specific volume measurements which were found to provide a very sensitive criterion of the state of the high speed steel. The first specimen was air-cooled from the tempering temperature each time, the second was oil-quenched, and the third was water quenched. From the results given in Table II, it appears that the tempering process is not materially affected by ordinary rates of cooling unless the cooling rate is very rapid. In the latter event, quenching strains probably accelerate the tempering process. Hence, the intermediate rate of oil cooling from the tempering temperature was adopted for all the specimens that were to be tested at room temperature.

Table II
Effect of Cooling Rate from the Tempering Temperature

Specimen No.	Specific Volume c.c./gm. 1	2	3
Annealed	0.11515	0.11517	0.11518
Hardened	0.11549	0.11546	0.11549
Tempered at 1000 degrees Fahr.	Air cooled	Oil quenched	Water quenched
0.5 hours	.....	0.11522	0.11527
1	0.11520	0.11520	0.11530
2.1	0.11546	0.11547	0.11551
6	0.11562	0.11562	0.11570
12	0.11565	0.11565	0.11575
24	0.11566	0.11566	.....
48	0.11567	0.11566	0.11574

Table III
Effect of Room Temperature Aging on Subsequent Tempering

Specimen No.	Specific Volume c.c./gm. 4	5
Hardened and aged 1 hour at 75 degrees Fahr.	0.11547	.....
Hardened and aged 600 hours at 75 degrees Fahr.	.....	0.11546
Tempered at 1000 degrees Fahr.		
0.5 hours	0.11520	0.11520
1	0.11521	0.11523
2.1	0.11547	0.11549
7	0.11558	0.11561
12	0.11566	0.11566
24	0.11565	0.11566
48	0.11569	0.11567

It was also important to ascertain the effect of room temperature aging prior to the tempering tests. Two hardened ½-inch cube specimens were tempered at 1000 degrees Fahr. (540 degrees Cent.) after having been aged previously at 75 degrees Fahr. for 1 hour and 600 hours respectively. The tempering of both specimens was repeatedly interrupted by oil quenching to room tempera-

ture for specific volume measurements. The results in Table III show no change during the room temperature aging, and no effect of this aging upon the subsequent tempering.

Discussion of Results

Mechanism of the Tempering Process—The X-ray photograms show that quenched high speed steel contains tetragonal martensite, residual austenite and undissolved carbides of the Fe_3W_3C type, probably best represented as $(Fe, W, Cr, V)_6 C$ (19). A total of 48 carbide lines were measured in the three X-ray photograms of the annealed high speed steel and, except for two very faint lines, they were all identified as belonging to the face-centered cubic structure described by Westgren and Phragmen (20) and by Gill (21) as Fe_3W_3C or Fe_4W_2C. After hardening, many of the weaker carbide lines disappear due to the partial solution of the carbides at the high heat temperature, but the positions of the remaining lines do not change as a result of hardening or tempering. The carbides in the annealed, quenched and tempered steels all have a lattice parameter value of 11.057 A.U. The tetragonal martensite is indicated by a doublet which appears in place of the usual (1 1 1)-α ferrite line, and which gives lattice parameter values of $a = 2.88$ A.U. and $c = 2.91$ A.U. with an axial ratio of 1.01. The only visible austenite line is the (1 1 1)-α line, but even this is partially obscured by the martensite doublet, so that the parameter of the austenite in the quenched steel cannot be measured satisfactorily.

However, during the early stages of tempering, this doublet merges into a broad body-centered cubic ferrite line, and the (1 1 1)-α austenite line becomes plainly visible. In addition, the (1 1 1)-β and the (2 0 0)-α austenite lines appear, presumably because of the relief of stresses in the austenite. It is estimated that there was 15 to 25 per cent austenite in the hardened high speed steel specimens used in this investigation.

A correlation of the tempering data shown in Figs. 2 to 8 reveals that the tempering mechanism involves at least four definite stages. The first stage consists of the decomposition of the tetragonal martensite, as indicated by the disappearance of the tetragonal doublet. This is accompanied by a marked softening, a decrease in volume, a decrease in electrical resistance, but no change in the

parameter of the austenite. This process occurs slowly on tempering at 212 to 350 degrees Fahr. (100 to 175 degrees Cent.), but becomes very rapid at the higher tempering temperatures. In fact, the rapid softening of the quenched martensite leads to the surmise that cementite, rather than the more stable complex carbide, precipitates from the tetragonal martensite, and quickly agglomerates.

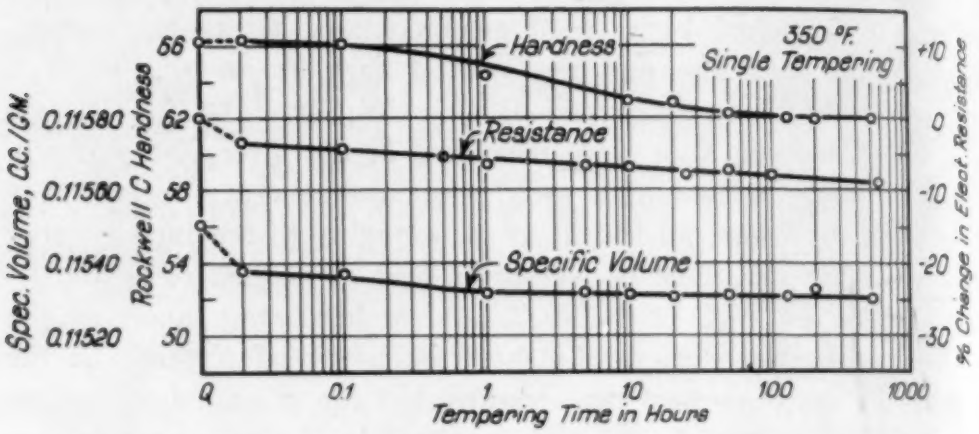


Fig. 2—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 350 Degrees Fahr. (175 Degrees Cent.).

To test this point, magnetization-temperature curves were determined for annealed and tempered high speed steel in order to detect the possible presence of a cementite Curie point. Cementite is ferromagnetic, but becomes paramagnetic when heated above its Curie point of 392 to 410 degrees Fahr. (200 to 210 degrees Cent.), thus causing a deflection in the magnetization-temperature curve in this temperature range. The detection of this Curie point in steel offers good evidence for the presence of cementite. No cementite Curie point was found in the annealed high speed steel, but a definite cementite Curie point was found at 374 to 392 degrees Fahr. (190 to 200 degrees Cent.) after hardening and tempering for one hour at 1050 degrees Fahr. In addition, Honda (22) has reported the presence of cementite in high speed steel after tempering at 500 degrees Fahr. (260 degrees Cent.). It may be deduced, therefore, that cementite (perhaps slightly alloyed) precipitates from the tetragonal martensite and rapidly agglomerates to cause the softening found during the first tempering stage. It is visualized that the urge for the supersaturated martensite to reject carbon is so great that it does so by the precipitation of the easily-formed cementite at tempering temperatures which are too low to allow sufficient dif-

fusion of the alloying elements for the occurrence of appreciable precipitation of the more stable complex carbide.

The second tempering stage is characterized by an increase in

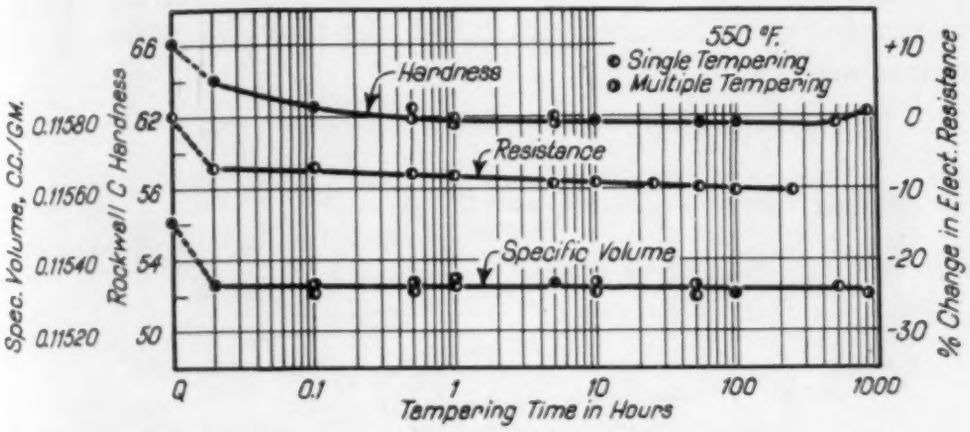


Fig. 3—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 550 Degrees Fahr. (290 Degrees Cent.).

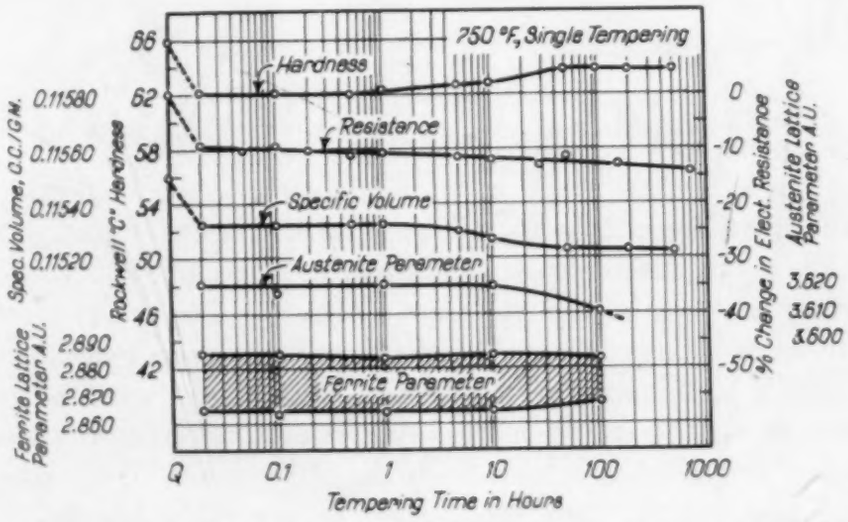


Fig. 4—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 750 Degrees Fahr. (400 Degrees Cent.).

hardness and a further decrease in the volume and electrical resistance. During this stage there is no consistent change in the ferrite diffraction lines, but the lattice parameter of the austenite begins to decrease, thus signifying a change in the composition of the austenite. Fortunately, it was noted that the alloy carbide lines in the No. 3 Phragmen photograms become slightly blurred at this time. Hence, the evidence is quite clear that the second tempering stage involves a precipitation from the retained austenite of alloy

carbides having about the same composition and structure as the undissolved complex carbides. This stage is evident in the tempering curves at 750, 900, 1000 and 1050 degrees Fahr. (400, 480, 540 and 565 degrees Cent.). At 1150 degrees Fahr. (620 degrees Cent.), the changes occur so rapidly that both the first and second stages are eclipsed.

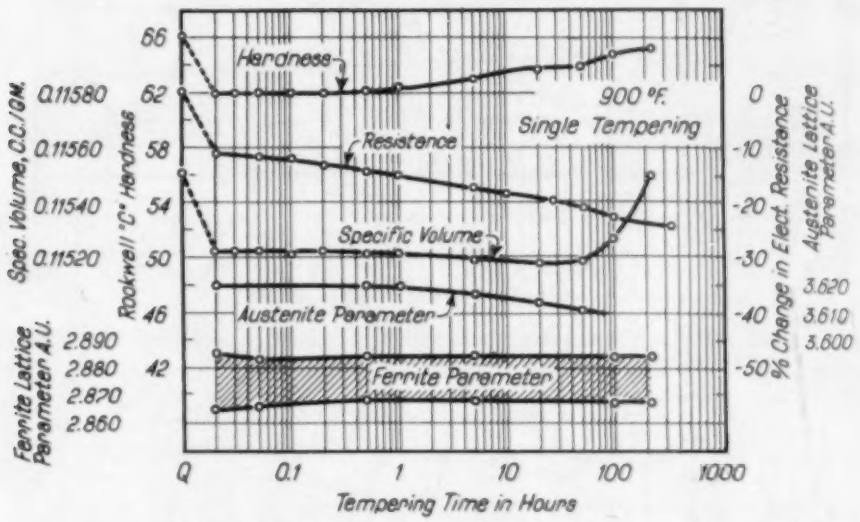


Fig. 5—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 900 Degrees Fahr. (480 Degrees Cent.).

The third stage consists of the transformation of the retained austenite, as is definitely proved by the decreasing intensity and final disappearance of the austenite diffraction lines. At the same time, there is a large expansion, a further increase in the hardness and a slight broadening of the ferrite lines. This stage is not attained in 500 hours at 750 degrees Fahr. but it is quite evident after tempering at the higher temperatures. It appears, then, that the retained austenite in high speed steel is very sluggish, but if its alloy and carbon contents are reduced by the precipitation of a sufficient amount of the complex carbide, the sluggishness of the austenite is lowered to the point where transformation results. After the austenite lines have disappeared and the specific volume reaches a maximum, the hardness begins to decrease slowly, presumably due to the softening of the products of the austenite decomposition and the continued coalescence of the cementite particles precipitated during the first stage.

The fact that the softening which follows secondary hardening takes place slowly as compared with the softening of the original

martensite in the quenched steel indicates that the transformation product of the retained austenite is based on alloy carbides rather than cementite. In the next section, evidence will be cited to show that this transformation product is most likely a tempered marten-

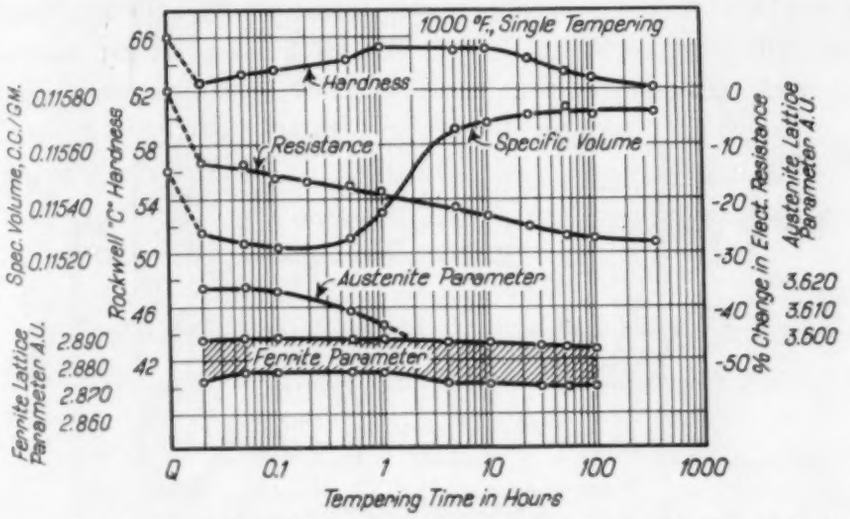


Fig. 6—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 1000 Degrees Fahr. (540 Degrees Cent.).

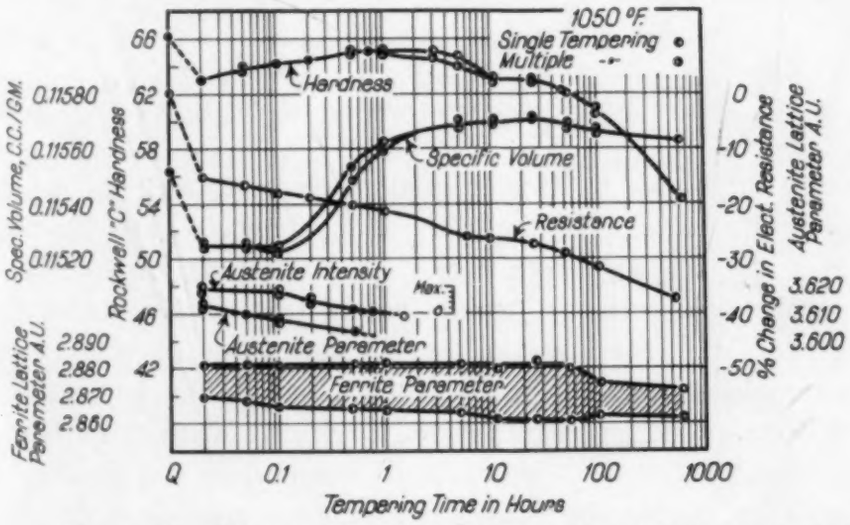


Fig. 7—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 1050 Degrees Fahr. (565 Degrees Cent.).

site. The complex carbides would be expected to grow slowly during tempering because such growth requires the simultaneous diffusion of the alloying elements as well as carbon, and therefore the secondary hardness is more persistent than the as-quenched hardness. This conception was clearly described by Bain and Jeffries over 15 years ago (23).

Finally, there is a fourth stage in which the ferrite lines first broaden perceptibly and then sharpen as the parameter begins to decrease. Here again the alloy carbide lines in the No. 3 Phragmen photograms are found to blur slightly. Consequently, the indications are that alloy carbides precipitate out of the ferrite matrix during this stage (nonuniformly at first to produce temporarily larger composition gradients in the ferrite than previously existed)

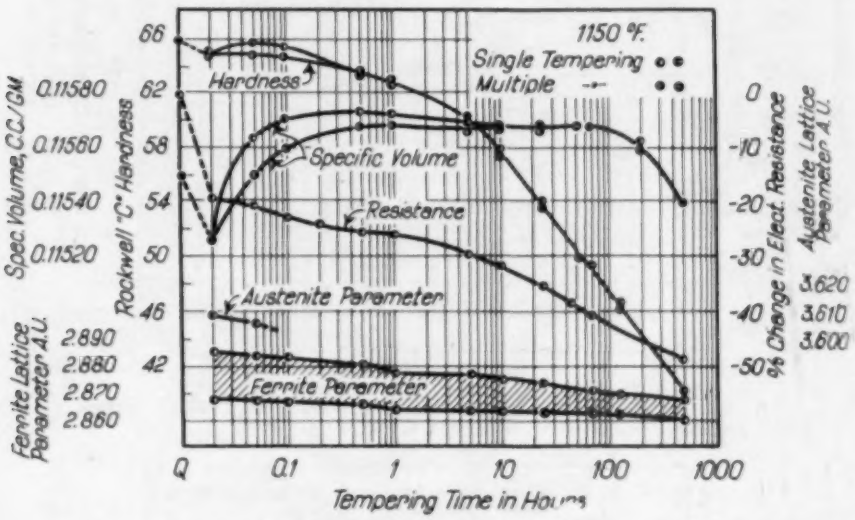


Fig. 8—The Effect of Tempering Quenched 18-4-1 High Speed Steel at 1150 Degrees Fahr. (620 Degrees Cent.).

and cause the lattice parameter of the ferrite, as well as the specific volume and resistance of the alloy as a whole, to shift towards the values in the annealed condition. This precipitation of alloy carbides probably contributes to the retardation of the softening following the secondary hardening. Hence, the alloying elements which remained dissolved in the ferrite (when the tetragonal martensite decomposed and precipitated cementite during the first tempering stage) ultimately come out of solution in the form of complex carbides during the fourth tempering stage. In order to provide carbon for the formation of these alloy carbides, it is believed that the less stable cementite gradually redissolves in the ferrite. Such a process may be inferred from the fact that when quenched high speed steel is tempered for a long time at 1150 degrees Fahr., it approaches the annealed condition, and annealed high speed steel does not show a cementite Curie point.

The changes in microstructure observed in this work add little to the metallographic studies already published (1), (4), (5). A

few typical structures are shown in Figs. 9 to 16. With nital etching, the matrix of the quenched steel appears homogeneous, but actually is a mixture of austenite and tetragonal martensite. The latter corresponds to the white martensite found in freshly quenched plain carbon steel, and explains why the characteristic acicular markings of martensite are not usually revealed in hardened high speed steel. However, the white martensite quickly darkens during the first stage of tempering because of the precipitation of carbides, and the acicular configuration appears after nital etching, but these carbides are apparently too finely divided to be detected by Murakami's reagent. This is also the case with tempered plain carbon steels. The second and third stages of tempering are accompanied by further darkening of the matrix until even the grain boundaries are practically obscured. Late in the fourth stage, the precipitated alloy carbides can be detected with Murakami's reagent.

The sequence of structural changes which occur during the tempering of high speed steel are summarized in Fig. 17. It should be emphasized that the four stages of tempering may overlap to a considerable degree, and that the fourth stage is not ordinarily encountered in the commercial tempering of high speed steel. Furthermore, it should be noted that secondary hardening is the result of a two-step process involving the precipitation of complex carbides from the residual austenite and the subsequent transformation of this austenite into a hard product.

The results of the multiple or intermittent tempering tests at 550, 1050 and 1150 degrees Fahr. (290, 565 and 620 degrees Cent.) are plotted with the results of the single tempering tests in Figs. 3, 7 and 8 respectively. No difference is noted between the two methods of tempering at 550 degrees Fahr., but at the two higher temperatures the multiple tempering yields a somewhat lower or less persistent secondary hardness and there is some divergence of the specific volume curves. Yet, the X-ray results after tempering at 1050 degrees Fahr. prove that the rate of carbide precipitation from the residual austenite and the rate of decomposition of the austenite are the same for both methods of tempering. This apparent discrepancy will be explained when the dilatometric results are discussed.

Kinetics of the Residual Austenite Transformation—Having shown the correspondence between the secondary hardening and the break-up of the retained austenite in high speed steel, it re-

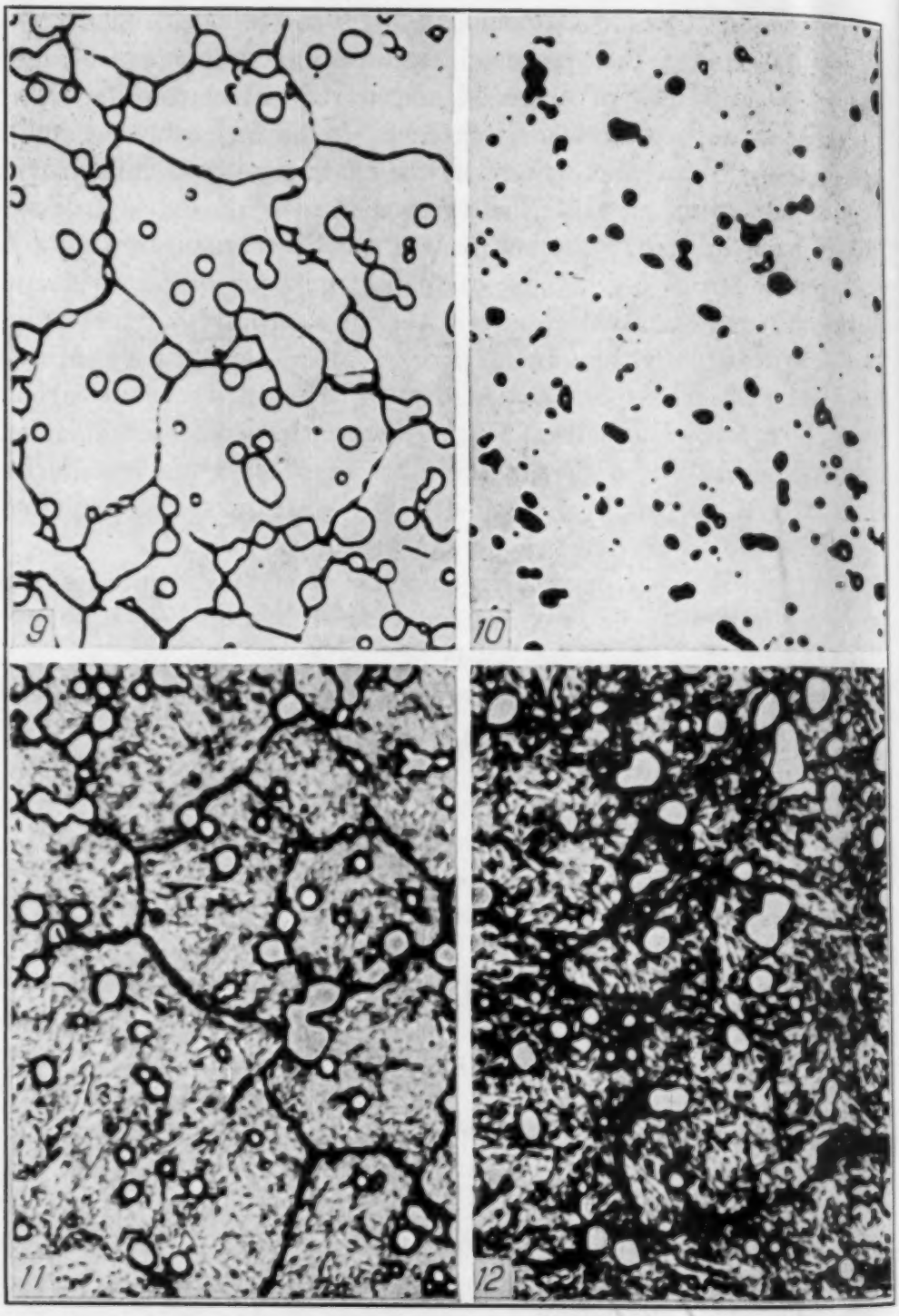


Fig. 9—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.). Grain Size 10. Two-Minute Etch with 6 Per Cent Nital. × 2000.

Fig. 10—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.). Fifteen-Minute Etch with Murakami's Reagent. × 1000.

Fig. 11—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.) and Tempered for 0.1 Hour at 900 Degrees Fahr. (480 Degrees Cent.). First Stage of Tempering. Two-Minute Etch with 6 Per Cent Nital. × 2000.

Fig. 12—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.) and Tempered for 10 Hours at 900 Degrees Fahr. (480 Degrees Cent.). Second Stage of Tempering. 2-Minute Etch with 6 Per Cent Nital. × 2000.

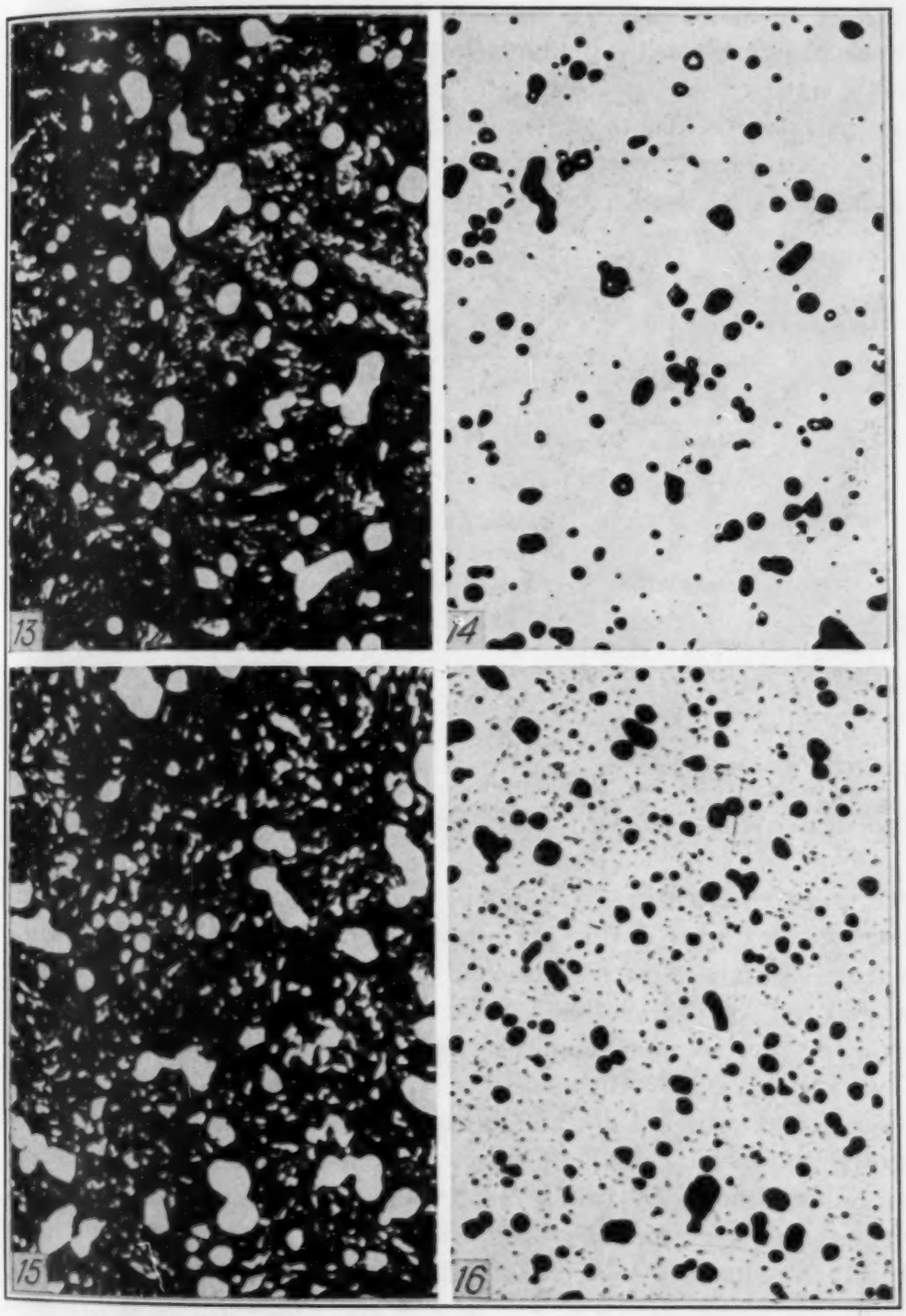


Fig. 13—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.) and Tempered for 2½ Hours at 1050 Degrees Fahr. (565 Degrees Cent.). Third Stage of Tempering. 2-Minute Etch with 6 Per Cent Nital. × 2000.

Fig. 14—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.) and Tempered for 2½ Hours at 1050 Degrees Fahr. (565 Degrees Cent.). Third Stage of Tempering. 15-Minute Etch with Murakami's Reagent. × 1000.

Fig. 15—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.) and Tempered for 69 Hours at 1150 Degrees Fahr. (620 Degrees Cent.). Fourth Stage of Tempering. 2-Minute Etch with 6 Per Cent Nital. × 2000.

Fig. 16—Microstructure of 18-4-1 High Speed Steel Hardened at 2350 Degrees Fahr. (1290 Degrees Cent.) and Tempered for 69 Hours at 1150 Degrees Fahr. (620 Degrees Cent.). Fourth Stage of Tempering. 15-Minute Etch with Murakami's Reagent. × 1000.

mained to investigate the kinetics of this transformation. This was done principally with dilatometric tests, and was confirmed by magnetic tests, since these techniques do not necessitate cooling to room temperature to obtain measurements.

According to the dilatometer curves at 350 and 550 degrees Fahr., a large contraction occurs during the decomposition of the

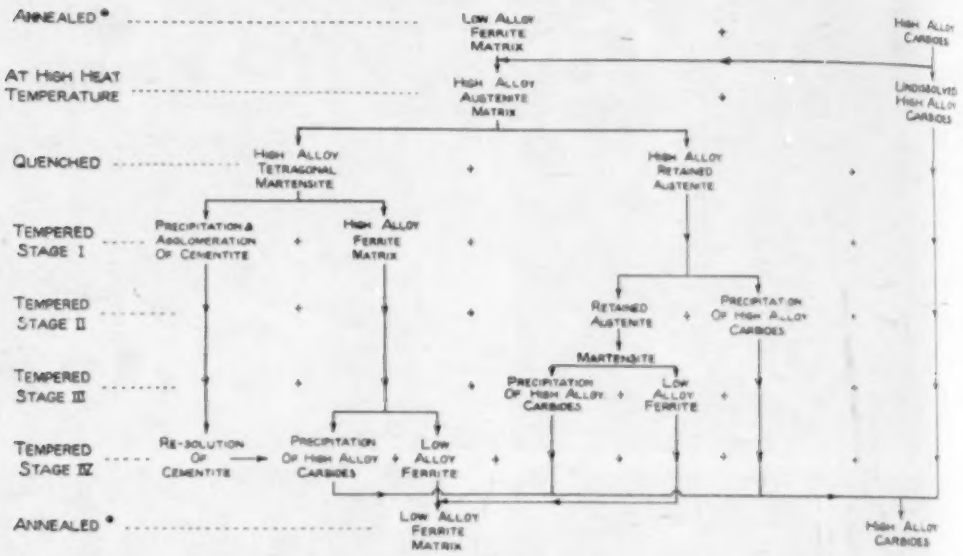


Fig. 17—Flow Sheet Showing the Probable Sequence of Structural Changes Which Occur in High Speed Steel. (*Grossmann and Bain (1) Have Shown That in Annealed High Speed Steel, the Bulk of the Alloying Elements are Associated with the Carbide Rather than with the Ferrite.)

tetragonal martensite. On tempering at higher temperatures, this contraction occurs during the heating, and is superimposed upon the normal heating-expansion curve (see Fig 18). During tempering at 750 and 900 degrees Fahr., a further contraction takes place which confirms the specific volume results obtained at room temperature. This corresponds to the second stage of tempering.

However, when the dilatometer runs are made at the higher temperatures for lengths of time sufficient to transform the residual austenite (on the basis of the previous room temperature measurements), no corresponding expansion occurs at the tempering temperature. Instead this expansion takes place during the cooling from the tempering treatment and is superimposed on the normal cooling-contraction curve. For example, the specific volume curve in Fig. 6 shows that the transformation of the residual austenite is virtually complete after tempering for 24 hours at 1000 degrees Fahr. The dilatometer curve in Fig. 19 demonstrates that holding

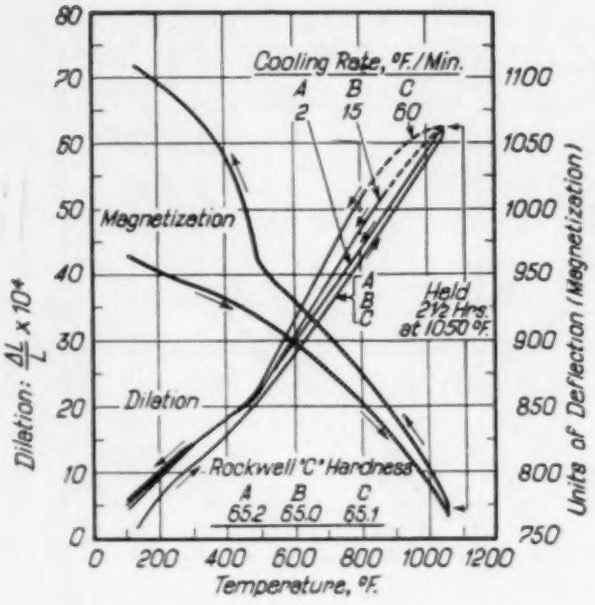


Fig. 18—Dilation and Magnetization-Temperature Curves Showing the Effect of Heating Quenched High Speed Steel to 1050 Degrees Fahr. (550 Degrees Cent.) for 2½ Hours and Then Cooling (at Three Different Rates in the Case of the Dilation Curves).

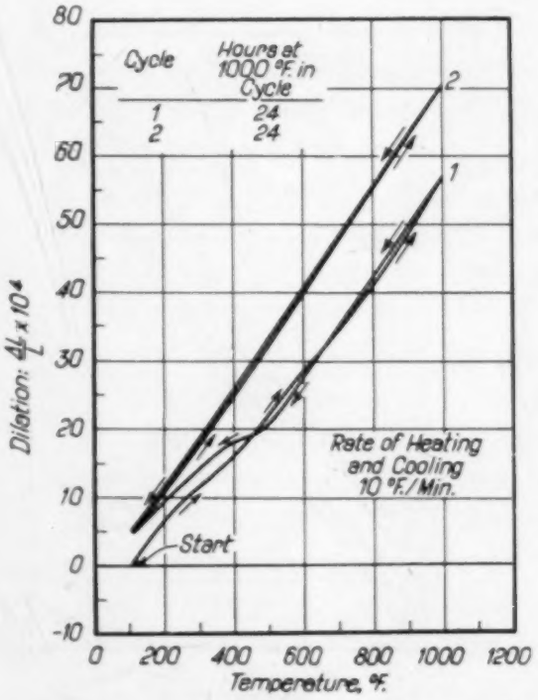


Fig. 19—Dilation Curves Showing Two Tempering Cycles. The Residual Austenite is Completely Transformed After the First Cycle: 24 Hours at 1000 Degrees Fahr. (540 Degrees Cent.).

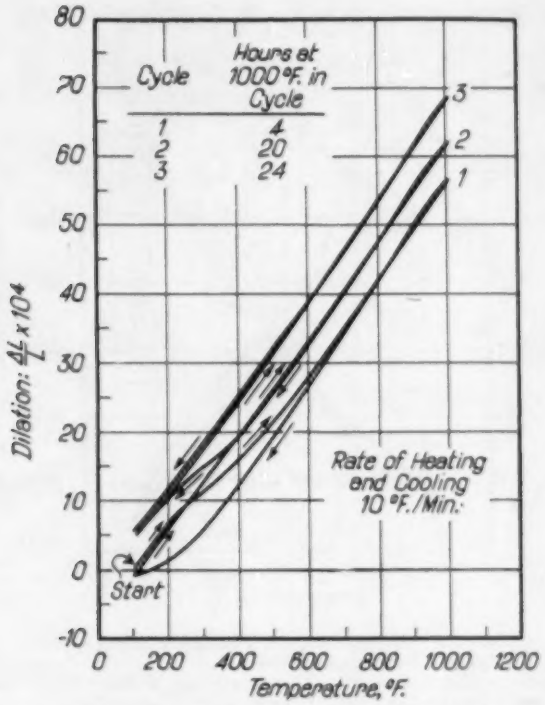


Fig. 20—Dilation Curves Showing Three Tempering Cycles. The Residual Austenite is Completely Transformed After the Second Cycle: 24 Hours at 1000 Degrees Fahr. (540 Degrees Cent.).

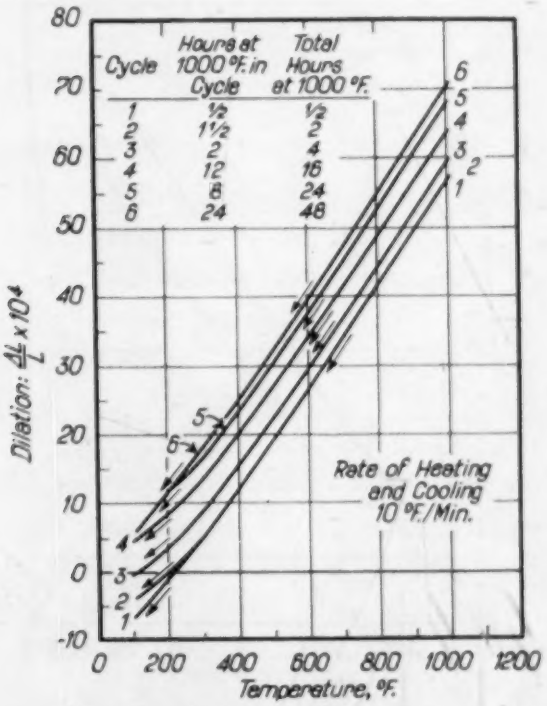


Fig. 21—Dilation Curves Showing Six Tempering Cycles. (The Heating Curves Are Not Included to Avoid Confusion). The Residual Austenite is Completely Transformed After the Fifth Cycle: 24 Hours at 1000 Degrees Fahr. (540 Degrees Cent.).

quenched high speed steel for 24 hours at 1000 degrees Fahr. produces no change in length at this temperature, but during the cooling after this treatment the austenite begins to transform at about 520 degrees Fahr. (270 degrees Cent.), and continues to transform as the temperature falls. In fact, the austenite transforms completely this way, as shown by the second cycle in Fig. 19 in which the same specimen is reheated to 1000 degrees Fahr. for 24 hours longer and is then cooled without any indication of further transformation. Thus it seems that the residual austenite transforms by a typical martensite or Ar″ reaction, rather than an isothermal decomposition at the tempering temperature.

This initial experiment which is in general agreement with the results of several foreign publications brings up many interesting questions. For example, if the residual austenite begins to transform at about 520 degrees Fahr. during cooling from the tempering temperature, why should not tempering at 550 and 750 degrees Fahr. cause the austenite to transform and produce secondary hardening? What is the effect of the rate of cooling on the temperature at which the transformation begins during cooling? Why should not the rate of cooling have a major effect on the amount of austenite which transforms, and the hardness which is attained? Why should not multiple or repeated tempering cause a more rapid break-up of the austenite than single tempering for an equal time? What is the relationship between the tempering treatment and the amount of austenite which subsequently transforms during cooling? What happens when the cooling is stopped before room temperature is reached? An attempt is made to answer these questions by the following experiments.

The effect of the rate of cooling from the tempering temperature is shown in Fig. 18 for three rates of cooling after tempering for 2½ hours at 1050 degrees Fahr. During this heating period, a small amount of austenite transforms at the tempering temperature as indicated by the slight isothermal expansion and the relatively small increase in the magnetization, but the bulk of the austenite transforms during the cooling, beginning at about 475 degrees Fahr. (245 degrees Cent.) in the dilatometer and magnetization curves. The austenite transformation is not noticeably suppressed by increasing the rate of cooling, nor is the Rockwell C hardness affected. (The initial bow in the cooling curves is due to the nonuniform cooling of the dilatometer parts.)

A comparison of Figs. 19, 20 and 21 demonstrates the effect of intermittent cooling and of tempering time on the austenite transformation. As mentioned previously, Fig. 19 shows that a single tempering treatment of 24 hours at 1000 degrees Fahr. produces complete transformation of the austenite on subsequent cooling. Fig. 20 shows that tempering at 1000 degrees Fahr. for 4 hours causes part of the austenite to transform during the cooling. A second treatment of 20 hours more (cumulative time at 1000 degrees Fahr = 24 hours) causes the rest of the austenite to transform during cooling, since a third treatment of 24 hours more at 1000 degrees Fahr. produces no further transformation. In Fig. 21, this experiment is repeated with six coolings. After only ½ hour at 1000 degrees Fahr. no austenite is found to transform even during cooling. However, after a second heating of 1½ hours (cumulative time at 1000 degrees Fahr. = 2 hours), a small part of the austenite transforms during cooling. A third heating of 2 hours (cumulative time at 1000 degrees Fahr. = 4 hours) and a fourth heating of 12 hours (cumulative time at 1000 degrees Fahr. = 16 hours) cause additional increments of austenite to transform during cooling. Finally, after a fifth heating of 8 hours (cumulative time at 1000 degrees Fahr. = 24 hours), the last of the austenite transforms during cooling. A sixth heating of 24 hours longer results in no further transformation. Similarly it is found (curves not shown) that substantially complete transformation of the austenite takes place during cooling when the steel is given a single temper of 2½ hours at 1050 degrees Fahr. or a double temper of 1 hour followed by 1½ hours, or a triple temper of 10 minutes followed by 50 minutes followed by 1½ hours. It appears, therefore, that in spite of the fact that the residual austenite transforms during cooling from the tempering temperature, the amount of austenite which transforms depends upon the tempering treatment and not upon the number of cooling cycles. This is in excellent agreement with the X-ray results shown in Fig. 7.

Since the amount of residual austenite which transforms during cooling is primarily dependent upon the "conditioning" which it receives during the tempering treatment, assuming, of course, that the composition of the steel and the hardening treatment are not introduced as variables, the time and temperature of tempering should have a pronounced effect on the beginning of the Ar″ trans-

formation. The set of dilatometer curves in Fig. 22 shows that the temperature of the beginning of this transformation is markedly raised by increasing the length of the tempering time at 1050 degrees Fahr. This is also found after tempering at 1000 degrees Fahr. and the results for both temperatures are summarized in Fig. 23. Very likely the raising of the Ar″ transformation range caused by increasing the time and temperature of the tempering treatment is due to the precipitation of the alloy carbides from the austenite. This precipitation was described as the second tempering stage on page 1025. Short tempering times and low tempering temperatures do not permit sufficient carbide precipitation to raise the Ar″ transformation range above room temperature, and hence the austenite does not transform after these treatments. The higher the Ar″ transformation range is raised by increasing the time and temperature of tempering, the sooner does the austenite begin to transform during cooling and the further advanced is the transformation by the time room temperature is reached. This explains the close connection between the tempering treatment and the amount of austenite which subsequently transforms.

A prolonged dilatometer run was made at 1150 degrees Fahr. (620 degrees Cent.) in order to determine whether the austenite would eventually undergo isothermal transformation. The curves in Fig. 24 show that the austenite completely transforms in 48 hours at this temperature, producing an isothermal expansion. Consequently there is no break in the cooling curve following this treatment. The hardness after this treatment is only Rc 50.2 which indicates that the isothermal transformation product is relatively soft. The isothermal transformation at 1150 degrees Fahr. begins in about 5 hours. Up to this time, cooling to room temperature causes the austenite to transform during the cooling. Heating for longer periods than 5 hours at 1150 degrees Fahr. causes increasing amounts of austenite to transform isothermally, and the remainder to transform during cooling. In Fig. 8, the hardness curve drops rapidly after 5 hours. This is probably due to the increasing amount of the isothermal transformation product.

The effect of stopping the cooling after the residual austenite begins to transform during cooling is shown by the dilatometer and magnetization curves in Fig. 25. Three dilatometer runs were made on identically hardened specimens. A was tempered for 2½ hours at 1050 degrees Fahr. in the dilatometer and was then cooled nor-

mally to room temperature. B and C were similarly treated except that the cooling was stopped for 1 hour and 20 hours respectively at 400 degrees Fahr. (205 degrees Cent.) before finally cooling to room temperature. The beginning of the Ar″ transformation occurred at about 475 degrees Fahr. (245 degrees Cent.) in the three

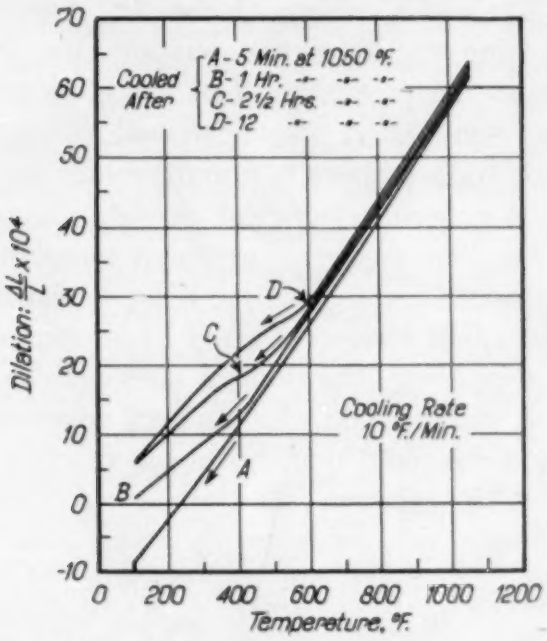


Fig. 22—Dilation Curves Showing the Effect of the Tempering Time at 1050 Degrees Fahr. (565 Degrees Cent.) on the Subsequent Transformation of the Austenite During Cooling.

specimens. The isothermal expansion in the B and C curves at 400 degrees Fahr. in Fig. 25 demonstrates that the austenite transforms even when the cooling is stopped. In fact, the transformation becomes complete in 20 hours at 400 degrees Fahr. as indicated by the subsequent cooling-contraction curve for specimen C. On the other hand, the austenite transformation does not complete itself in 1 hour. During the subsequent (continuous) cooling of specimen B from 400 degrees Fahr., there is little, if any, transformation of the remaining austenite through a temperature drop of about 50 degrees Fahr., after which the austenitic transformation sets in almost as though the cooling had not been interrupted at 400 degrees Fahr. It seems that a 1-hour treatment at 400 degrees Fahr. (after cooling from a 2½-hour temper at 1050 degrees Fahr.) destroys that part of the austenite which would have transformed during cooling between 400 and 350 degrees Fahr. if the cooling had not been stopped at 400 degrees Fahr. By further increasing the holding time

at 400 degrees Fahr., the extent of the isothermal transformation is increased and the greater is the temperature lag during subsequent cooling before the rest of the austenite begins to transform.

The hardness values of the above three specimens (A = Rc 65.1, B = Rc 64.2, and C = Rc 63.0) signify that the transforma-

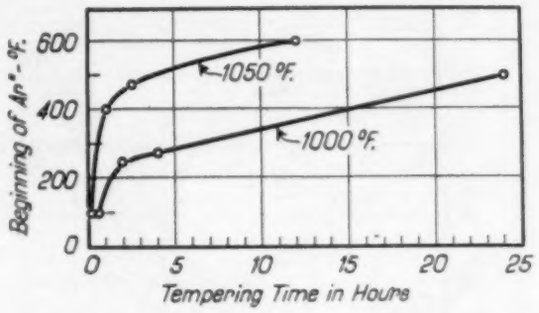


Fig. 23—The Influence of the Time of Tempering at 1000 and 1050 Degrees Fahr. (540 and 565 Degrees Cent.) on the Beginning of the Ar" Transformation During Subsequent Cooling.

tion product of the isothermal transformation is appreciably softer than the product resulting from the transformation during cooling. This softer product is not the result of a tempering action at the holding temperature of 400 degrees Fahr., as shown by a simple experiment. A specimen was tempered at 550 degrees Fahr. after being previously tempered at 1050 degrees Fahr. for 2½ hours, and the hardness results as shown in Table IV were obtained at room temperature.

Table IV

Effect of Retempering at 550 Degrees Fahr. After Tempering at 1050 Degrees Fahr.

	Rc Hardness
Tempered at 1050° F. for 2½ hours	65.1
Retempered at 550° F. for 0.02 hour	64.7
Retempered at 550° F. for 0.1 hour	64.8
Retempered at 550° F. for 1 hour	64.7
Retempered at 550° F. for 24 hours	64.7

These data demonstrate that if the residual austenite transforms into its usual hard product during cooling to room temperature, this product is barely softened by tempering even above 400 degrees Fahr. Yet, the product which forms directly from the austenite when the cooling is stopped at 400 degrees Fahr. is definitely softer.

Using the hardness as a rough criterion of the extent of this isothermal transformation, the data in Table V suggest that the

isothermal transformation of the austenite (after tempering at 1050 degrees Fahr. for 2½ hours) may occur even when the cooling is stopped above the usual Ar″ transformation temperature of 475 degrees Fahr., but the isothermal transformation is most rapid (and hence results in lowest hardness) just below the Ar″ tem-

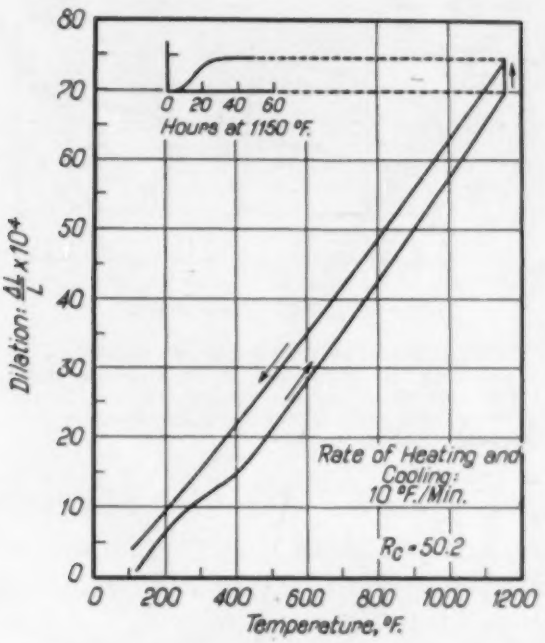


Fig. 24—Dilation Curves Showing the Isothermal Transformation of Residual Austenite at 1150 Degrees Fahr. (620 Degrees Cent.).

perature. The high hardness obtained after holding at 200 degrees Fahr. is due to the fact that practically all of the austenite is transformed during the cooling before this temperature is reached.

Table V

Hardness Values of Specimens Tempered for 2½ Hours at 1050 Degrees Fahr. and Then Cooled as Follows:

	Rc Hardness
Cooling interrupted at 700° F. for 20 hours	65.0
Cooling interrupted at 640° F. for 20 hours	64.6
Cooling interrupted at 500° F. for 20 hours	63.8
Cooling interrupted at 400° F. for 20 hours	63.0
Cooling interrupted at 300° F. for 20 hours	64.0
Cooling interrupted at 200° F. for 20 hours	65.1
Furnace-cooled to room temperature (4° F./hour)	65.0
Air-cooled to room temperature	65.2
Oil-quenched to room temperature	65.1

The high hardness obtained after furnace, air and oil cooling from 1050 degrees Fahr. shows that if the cooling is continuous, the iso-

thermal transformation does not seem to occur even if the cooling rate is very slow.

On the basis of these results, it is evident that the residual austenite transformation which occurs during cooling after the proper tempering treatment is a true martensitic reaction. This accounts for the slight broadening of the ferrite diffraction lines during the third stage of tempering. However, the martensite thus

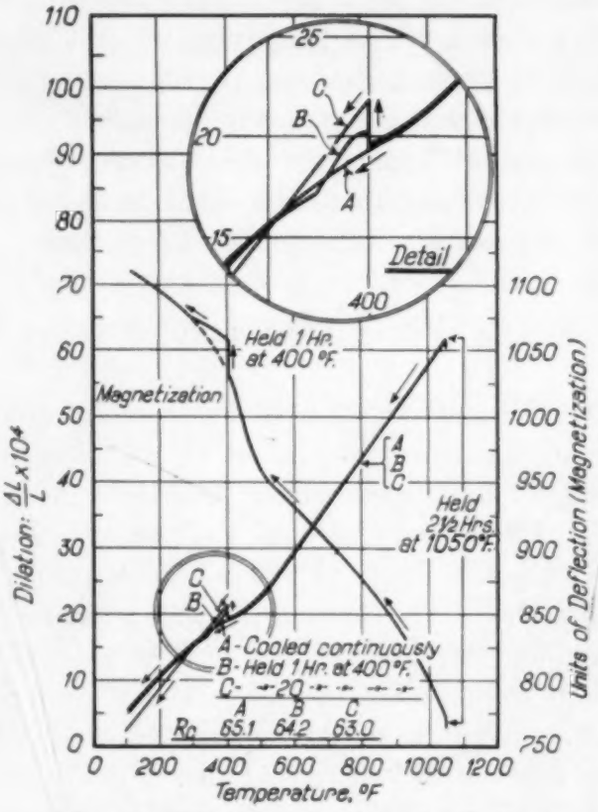


Fig. 25—Dilation and Magnetization-Temperature Curves Showing the Effect of Stopping the Cooling at 400 Degrees Fahr. (205 Degrees Cent.) After Heating Hardened High Speed Steel at 1050 Degrees Fahr. (565 Degrees Cent.) for 2½ Hours.

formed differs markedly from the original martensite in the quenched steel since further tempering after the secondary hardening causes very slow softening as compared to the rapid drop in hardness produced by tempering the original martensite. As mentioned on page 1027, it is believed that the second martensite precipitates alloy carbides, instead of cementite, during subsequent tempering or heating in service, and the sluggish growth of these alloy carbides retards the softening of the steel.

The slight differences in the hardness and specific volume meas-

urements as produced by single and multiple tempering at 1050 and 1150 degrees Fahr. (Figs. 7 and 8) are now readily explained. During the third tempering stage, the single tempering hardness curve lies above the multiple tempering hardness curve because with the former method of tempering, the martensite forms during the cooling after the exposure to the tempering temperature; whereas in the latter method of tempering, the increments of martensite formed during the successive coolings are slightly softened by the subsequent tempering cycles. The tempering of this martensite would also be expected to cause a decrease in volume, which accounts for the fact that multiple tempering yields lower specific volume values than single tempering during the third stage of tempering even though the cumulative amount of residual austenite transformed is independent of the number of intermittent coolings.

Practical Aspects of the Tempering of High Speed Steel

This mode of transformation of the residual austenite has distinct practical significance and should be taken into consideration in the tempering of high speed steel. Consider the case of a hardened 18-4-1 high speed steel tool[4] which is normally given a 2½-hour temper at 1050 degrees Fahr. to attain secondary hardness and relieve quenching stresses. If the tool is given a single 2½-hour treatment, the quenching stresses are relieved (in the practical sense of the phrase), but virtually all of the retained austenite transforms during the cooling from the tempering temperature. This Ar″ transformation occurs below 475 degrees Fahr. and is accompanied by a marked expansion. Since the interior of the tool cools more slowly than the surface layers, the interior goes through the Ar″ temperature range later than the surface layers, and hence continues to expand after the austenite transformation at the surface is complete. This sets up high tensile stresses in the outer fibers and compressive stresses in the core, which may cause undue brittleness of the tool, as well as a gradual change in the dimensions of the finish-ground tool on standing at room temperature or during service. This gradual movement in finished high speed steel tools is troublesome and yet is frequently encountered. If a 4-hour tempering treatment is used, the residual austenite again transforms during

[4]Assume that the tool was hardened like the specimens in this investigation so that the present tempering data may be applied.

the cooling, and once more the internal stresses are introduced. On the other hand, suppose multiple tempering is used. If the tool is tempered first for 1 hour, about 80 per cent[5] of the residual austenite transforms during cooling to cause internal stresses again. However, when the tool is tempered a second time for 1½ hours (cumulative time at 1050 degrees Fahr. = 2½ hours), these stresses are relieved and the martensite formed during the first tempering cycle is slightly softened and toughened. During the cooling after the second tempering, the remaining 20 per cent of the austenite transforms into martensite, but, of course, the stress condition is much less acute than after the single tempering. By tempering a third time at 1050 degrees Fahr. or even below, even these lesser stresses may be relieved and the second increment of martensite is toughened. Thus, the advantage of multiple tempering over single tempering lies in the relief of stresses and the drawing of the martensite formed during the cooling after previous tempering treatments.

Along these lines, it has been observed that high speed steel tools, such as broaches, are more difficult to "cold-straighten" without breaking after multiple tempering than after single tempering. This seems contradictory since it was just shown that multiple tempering should produce greater toughness and slightly lower hardness than single tempering. However, it is important to note that cold straightening is not done cold, but during cooling from the tempering temperature in the range of 900-600 degrees Fahr. (This cold straightening operation is so named to distinguish it from the hot straightening which is usually carried out during the quench from the high heat temperature.) Since the residual austenite does not transform until the temperature drops below 475 degrees (approximately), it follows that the cold straightening after single tempering is actually done while the (relatively soft and ductile) residual austenite is still present in the steel. On the other hand, if the straightening is attempted after multiple tempering, the residual austenite has already been transformed during the previous coolings and hence the straightening must be accomplished on the steel in its secondary hardened state, which, of course, is stronger, more brittle, and more resistant to straightening than when the residual austenite is present. However, this difficulty, when multiple tempering is used, may be avoided by performing the straightening dur-

[5]Calculated from change in specific volume.

ing the cooling from the first, instead of the last, tempering treatment.

While it has been demonstrated that the rate of cooling following the tempering has little effect upon the austenite transformation and the final hardness, it should be borne in mind that internal stresses are introduced during the cooling because of the expansion due to the residual austenite transformation. These internal stresses are exaggerated by rapid cooling because the temperature gradients cause the austenite transformation to proceed nonuniformly. By the same token, very slow cooling from the tempering temperature should minimize the nonuniformity of the transformation and thus prevent the building up of such high stresses. At the same time, it has been shown that very slow cooling rates do not result in any sacrifice of the secondary hardness. However, the cooling, slow as it may be, must be continuous: if the cooling is stopped within a certain temperature range, the austenite will transform isothermally into a softer product than is normally produced as a result of continuous cooling.

Conclusions

1. Hardened 18-4-1 high speed steel contains highly alloyed tetragonal martensite, highly alloyed retained austenite, and undissolved complex carbides.

2. The general tempering mechanism of hardened high speed steel involves four overlapping stages:

I. Decomposition of the tetragonal martensite with the precipitation and coalescence of cementite in a highly alloyed ferrite matrix.

II. Precipitation of complex carbides from the residual austenite.

III. Transformation of the residual austenite.

IV. Precipitation of complex carbides from the ferrite matrix of stage I, and the re-solution of the cementite.

3. The initial softening of hardened high speed steel is due to stage I. The secondary hardening results from a combination of stages II and III. Stage IV is not encountered in normal commercial tempering.

4. In normal heat treatment, little, if any, of the residual austenite transforms at the tempering temperature. Instead it transforms during cooling into martensite which is probably based on

complex carbides rather than on cementite and hence is more resistant to softening than the original martensite.

5. The amount of austenite which thus transforms and the temperature at which this transformation begins during cooling depend principally upon the time and temperature of tempering, assuming constant hardening conditions, and seem to be independent of the cooling rate unless the latter is rapid enough to introduce quenching stresses. Furthermore, the cumulative amount of austenite transformed after a given time of tempering is independent of the number of intermittent coolings to room temperature.

6. The residual austenite may transform isothermally if the cooling from the tempering temperature is stopped within the proper temperature range. The product of this isothermal transformation is softer than the martensite formed during the continuous cooling of the austenite.

7. The transformation of the residual austenite into martensite during cooling after tempering causes an appreciable expansion at fairly low temperatures, and hence results in internal stresses. Using longer times of (single) tempering does not remove these stresses because the austenite still transforms during the cooling. On the other hand, if multiple tempering is used, the austenite transforms into martensite in increments during successive coolings so that the stresses are relieved and the martensite is toughened by the subsequent heatings. For the same reason, multiple tempering may result in slightly lower secondary hardness than the single tempering.

8. Prolonged tempering at 1150 degrees Fahr. (620 degrees Cent.) causes the austenite to transform isothermally at the tempering temperature, but the transformation product is relatively soft.

Acknowledgments

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DISCUSSION

Written Discussion: By Robert S. Rose, sales representative, Vanadium-Alloys Steel Co., Boston.

It has been indeed a pleasure to read this paper deliberately narrow in scope and so excellently conceived and scientifically conducted. The results obtained have both technological and practical significance. There is, I believe, the first conclusive proof in an American paper that the transformation of retained austenite in as-quenched high speed steel occurs during the cooling from rather than isothermally at the tempering temperature. A knowledge of this is a prerequisite to understanding the cause of the improved mechanical properties obtained by multiple tempering. Of equal importance, it seems to me, are the improved properties likely to be realized by causing the transformation to take place isothermally at approximately 400 degrees Fahr. rather than by continuous cooling even though the holding time may be somewhat less than 20 hours. Fig. 25 indicates the product of transformation at 400 degrees Fahr. is less voluminous and less hard. Thus this method has the advantage of inducing less volume change and less stress in a temperature range in which the steel is better able to accommodate itself than during ordinary continuous cooling. There are many high speed steel applications that do not demand maximum hardness.

The many methods employed to follow the tempering reactions seem to confirm and complement each other. The final disappearance of the austenite intensity line after holding 2½ hours at 1050 degrees Fahr. as shown in Fig. 7 gives a final answer to an old argument. The breakdown of this austenite prior to that of ferrite seems at first anomalous since the reverse is true with carbon and low alloy steels. Upon analysis, however, the ferrite which remains after the precipitation of cementite can well be a carbon-free stable ferrite in which tungsten-chromium and vanadium have specific solvency. Carbon from cementite would redissolve in increasing amounts with temperature and thus provide that necessary for subsequent precipitation of alloy carbides.

Written Discussion: By W. E. Bancroft, chief metallurgist, Pratt & Whitney Co., Hartford, Conn.

I think the authors of this paper are to be highly congratulated and thanked for this valuable and enlightening paper. Their discoveries and conclusions regarding the behavior of hardened high speed steel during quenching serve to confirm and explain in a satisfactory manner some of the phenomena which tool manufacturers have been noticing and making use of to a greater or lesser degree for some time, but which they did not, in all cases, thoroughly understand.

From the standpoint of a manufacturer of high speed steel cutting tools, it is illuminating to read such a clear and reasonable explanation of the benefits to be derived from multiple tempering. This has been a debatable point among tool manufacturers for some time. I feel that the explanation of what takes place, which is presented in this paper, is satisfactory and conclusive and should serve to clear up the lack of agreement on this point. In this connection I note the authors state that the third draw does not need to be at the secondary hardening temperature. I believe that a low draw at a temperature of say 500 to 700 degrees Fahr. would be sufficient to relieve most of the stresses present without any noticeable further tempering of the martensite and consequent reduction in hardness.

The authors' discoveries regarding the effect of total time at tempering temperature on the amount of austenite transformed are quite interesting and valuable. They have shown that at 1000 degrees Fahr. 24 hours is necessary to produce complete transformation, and at 1050 degrees Fahr. only 2½ hours total time is necessary. It would be interesting to see these same data worked out for other temperatures between 1050 and 1150 degrees Fahr.

The authors are to be commended for their carefully worked out flow sheet showing the sequence of structural changes which take place in hardening high speed steel. If future experimental work and practical experience do not upset this arrangement this chart should come to occupy an important place in the reference literature of any laboratory concerned with the heat treating of high speed steel.

Oral Discussion

W. R. FRAZER:[1] Mr. Cohen is to be congratulated on his very splendid fundamental study of the phenomena which take place during the tempering of high speed steel, and, speaking for those of us who are daily engaged in hardening and tempering high speed tools, we should welcome this very timely investigation by two very energetic young men, primarily because they are associated with an institution which is equipped to study these problems from a theoretical standpoint, and thereby confirm some of the things which we have learned through the more difficult road of experience.

There are some things that I would like to inquire about, and one of them is the question of hardness which results from single versus repeated temperings. The curves do not bring out distinctly the degree of hardness difference, as the circles overlap each other. If we consider Fig. 7, which shows the hardness values with single tempering and multiple tempering: at one hour, there is less than half a point in Rockwell difference, and with three hours there might be one point in Rockwell difference. It is a little confusing, and I would like to ask Mr. Cohen if he has some actual tabular data showing exactly what the difference in hardness is. Practically speaking, I do not think that we find this to be true. Repeated temperings usually will show Rockwell hardness values equal to single tempering, but, of course, that probably is related to the analysis of the steel and to the carbide distribution.

I notice that the composition of the steel used for the hardness studies

[1]Metallurgist, Union Twist Drill Co., Athol, Mass.

shows 0.72 carbon, 17.84 tungsten, 3.92 chromium and 0.98 vanadium. The tungsten, chromium and vanadium are all on the low side of the specification for 18-4-1 high speed steel and this may account for the lower hardness after repeat tempering obtained by the authors. From our studies we feel that vanadium is a very potent element in controlling hardenability, and I might ask Mr. Cohen if he has made any study of an 18-4-2 steel to determine the effectiveness of vanadium on this property.

Mr. Cohen is to be congratulated and I hope that he will continue his investigations to give us further fundamental information on this subject.

FRANCIS B. FOLEY:[2] This thorough investigation of the nature of the changes which take place during the tempering of high speed steels explains in a very large degree the reason for the behavior of high speed steels which we have observed in commercial practice during a number of years. The interpretation which the authors place on their data seems to me quite sound.

This work shows that it may frequently repay the hardener of high speed steels to give some attention to the cooling rate following tempering of high speed steels. The factor of speed of cooling from the drawing temperature becomes more important as the size of the tools increases. I recall a few years ago, how a long piece of 2-inch by 4-inch section of high speed steel containing cobalt started cracking about 12 hours after it had been drawn twice and permitted to cool in air after each drawing and that a second piece treated in the same manner but cooled slowly in a furnace showed no cracks whatever.

High speed steels crack more frequently in the drawing operation than they do in hardening due to this volume change which the authors show so clearly to take place at low temperatures during cooling from the drawing temperatures.

From the practical point of view this work shows the importance of controlling the rate of cooling of large tools, particularly those having sharp corners at which stresses, created by the volume change at low temperature, may concentrate.

Authors' Reply

Mr. Rose has called attention to the possibility of obtaining improved properties in high speed steel by allowing the retained austenite to transform isothermally at 400 degrees Fahr. after cooling from the tempering temperature. This very thought occurred to the authors some time ago, and tests are now under way at the institute to determine (1) the factors which control this isothermal transformation, (2) the mechanical properties of the isothermal transformation product and (3) the effect of this type of heat treatment on the service-life of high speed steel dies subjected to repeated impact. The authors are pleased to note that Mr. Rose anticipates some commercial application of this low temperature isothermal treatment of high speed steel.

Mr. Foley's remarks concerning the cracking of high speed steel during the cooling from the tempering temperature are quite in line with our own experiences. During the early stages of our research, we were surprised to find that cracking of our specimens occurred more frequently during cooling

[2]Superintendent, research department, The Midvale Co., Nicetown, Philadelphia.

from the tempering temperature of 1050 degrees Fahr. than during cooling from the hardening temperature of 2350 degrees Fahr. The cause of this anomaly is now readily explained in the light of the present paper. During the quench from the high heat temperature, the martensite forms in a surrounding structure that is predominantly austenitic. Because of the plasticity of the untransformed austenite, the steel is able to adjust itself to the volume changes which accompany the formation of the martensite. However, when the retained austenite transforms into martensite during the cooling from the tempering temperature, the matrix of the steel is largely composed of (tempered) martensite. Due to the high elastic limit and low plasticity of this environment in which the new martensite forms, even moderate rates of cooling from the tempering temperature may lead to severe internal stresses and cracking. As Mr. Foley suggests, the present investigation brings out the importance of cooling slowly from the tempering temperature. This is particularly true in the case of large complicated tools with sharp corners.

Mr. Bancroft has inquired about the relationship between the tempering temperature and the tempering time necessary to produce complete transformation of the retained austenite during subsequent cooling. We can supply information for three tempering temperatures: 24 hours at 1000 degrees Fahr., 2½ hours at 1050 degrees Fahr., and about 10 minutes at 1150 degrees Fahr. It should be noted that these times represent "time at temperature" since small specimens and liquid baths were used for all the tempering treatments in this investigation. If any of these data are to be applied to commercial tempering where large specimens are treated in air furnaces, the time to reach the tempering temperature must be taken into consideration. Furthermore, the authors wish to call attention to the fact that these tempering times will vary with the composition of the high speed steel and with the high heat treatment used.

The authors quite agree with Dr. Frazer that "practically speaking" both single and multiple tempering produce about the same maximum secondary hardening. This comparison was one of the original purposes of the present investigation. Some previous Russian work indicated that multiple tempering might yield considerably higher secondary hardness than single tempering for an equivalent length of time. Our work showed no such advantage for multiple tempering. At 1050 degrees Fahr. both methods of

Rockwell C Hardness Attained on Tempering at 1050 Degrees Fahr.

Time of Tempering	Single Tempering	Multiple Tempering
As hardened	66.0	66.0
.02 hour	63.1	63.1
.05	63.9	63.6
.1	64.2	64.2
.2	64.4	64.4
.5	65.2	65.0
.75	65.1	65.1
1.0	65.3	64.9
3.0	65.2	64.6
5.0	64.8	64.1
11.0	63.2	63.0

tempering resulted in about the same maximum secondary hardness, but this hardness was retained for longer periods of time when single tempering was used. At a tempering temperature of 1150 degrees Fahr. which is higher than is normally used in commercial practice, the secondary hardening was greater in the case of the single tempering. The preceding table offers a comparison of the two types of tempering at 1050 degrees Fahr.

The differences in the hardness values produced by the two methods of tempering are very small, perhaps insignificant for most practical purposes; but in our work where the heat treatment and measurements were carried out under carefully controlled conditions, these small differences were detected consistently, and can be nicely explained by the mechanism of tempering as described in this paper.

In reply to Dr. Frazer's question concerning the vanadium content of the high speed steels studied, we purposely confined our attention to the 18-4-1 composition in order to make our investigation as intensive as possible. We are of the opinion that the basic mechanism of the tempering process would not be affected materially by appreciable changes in the vanadium content of the high speed steel even though the mechanical properties and hardness-time-temperature relationships might vary considerably with the vanadium content.

DRAWING OF ALUMINUM

By L. J. Weber and J. T. Weinzierl

Abstract

The drawing of aluminum is discussed from the viewpoint of the tool designer as well as the man in the shop. Various shapes are considered and drawings of the operations are given for forming these shapes. Besides tool design, other factors such as lubrication, press setup and metallurgical aspects of the sheet are also discussed. Data is given to show the effect of drawing on the mechanical properties and their relation to tool design. The principles of drawing outlined for aluminum may also hold for other metals and alloys such as brass and steel. It is hoped that others will discuss this subject and thus add to our knowledge of forming sheet in draw presses.

Introduction

THE forming of sheet in draw presses has been discussed to a considerable extent in the literature but in most cases the data presented are of little value to the man who designs the tools or the foreman who is responsible for the production of satisfactory drawn shells. Since the aims of this Society are to help the men in the plant with their problems as well as to increase our knowledge of metals, it was thought desirable to discuss the drawing of sheet from a practical viewpoint and at the same time present our ideas on the metallurgical aspects that influence the results that are obtained. Our experience has been confined mainly to aluminum and its alloys. The data presented are therefore directly applicable to this metal and its alloys. With slight modifications the data as well as the underlying principles should also hold true for other metals and alloys.

Presses Used for Drawing Aluminum

The presses required for drawing aluminum are the same as

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Table I
Capacity of Presses Used for Drawing Various Sizes of Blanks

Type of Press	Capacity	Maximum Diameter of Shell Inches	Maximum Thickness of Blank Inches	Max. Depth of Draw Inches
Double Action Toggle	63 Tons	8⅞	0.051	4¾
Double Action Toggle	125 Tons	14	0.102	8½
Double Action Toggle	148 Tons	15½	0.102	9½
Double Action Toggle	282 Tons	23	0.125	10
Double Action Toggle	300 Tons	27	0.125	10
Double Action Toggle	360 Tons	25	0.125	14½
Double Action Toggle	400 Tons	30	0.156	12
Double Action Toggle	550 Tons	30	0.187	17
Double Action Toggle	500 Tons	37	0.250	14
Hydraulic	1300 Tons	49	0.3125	24

those used for other metals. The size and capacity of the press will depend on the following factors.

1. Diameter of blank
2. Thickness of metal
3. Shape of the drawn item
4. Alloy and temper.

In case of trays or similar articles in which there is a large flat area, a suitable air cushion mounted in the press is preferred to springs or rubber pads placed in the draw tools, to supply the pressure which will prevent buckling and retain the flatness of the sheet.

The approximate sizes of blanks that can be drawn on various sizes of presses are given in Table I. The figures given are not to be considered as definite limits, but rather as the limits that have been found to be approximately correct from actual experience.

Alloys of Aluminum Used for Drawn Items

At the present time five alloys are generally used for the production of drawn shapes. These are designated by the Aluminum Company of America as 2S, 3S, 4S, 52S and 53S. The first four are generally referred to as "common alloys" as their mechanical properties can be increased only by cold work. The temper is designated as "O" for annealed sheet, "H" for full hard and "¼H or ½H" for intermediate tempers. The 53S alloy is referred to as a heat treatable alloy since it contains a constituent that makes possible a change in properties by heat treatment. The soft or annealed temper is designated as "O", the temper obtained by quenching from 960 degrees Fahr. in cold water and aged only at room temperature

Table II
Mechanical Properties and Composition of Aluminum Alloys

Alloy and Temper	Ultimate Strength Lbs. Per Sq. In.	Yield Strength Lbs. Per Sq. In.	Elongation Per Cent in 2 In.	Brinell Hardness	Composition*			
					Si	Mn	Mg	Cr
2S-O	13,000	5,000	35.00	23	....	....	....	....
2S-¼H	15,000	13,000	12.0	28	....	....	....	....
2S-½H	17,000	14,000	9.0	32	....	....	....	....
2S-H	24,000	21,000	5.0	44	....	....	....	....
3S-O	16,000	6,000	30.0	28	....	1.25	....	....
3S-¼H	18,000	15,000	10.0	35	....	1.25	....	....
3S-½H	21,000	18,000	8.0	40	....	1.25	....	....
3S-H	29,000	25,000	4.0	55	....	1.25	....	....
4S-O	26,000	10,000	20.0	45	....	1.25	1.0	....
4S-¼H	31,000	22,000	10.0	52	....	1.25	1.0	....
4S-½H	34,000	27,000	9.0	63	....	1.25	1.0	....
4S-H	40,000	34,000	5.0	77	....	1.25	1.0	....
52S-O	29,000	14,000	25.0	45	....	....	2.5	0.25
52S-¼H	34,000	26,000	12.0	62	....	....	2.5	0.25
52S-½H	37,000	29,000	10.0	67	....	....	2.5	0.25
52S-H	41,000	36,000	7.0	85	....	....	2.5	0.25
53S-O	16,000	7,000	25.0	26	0.7	....	1.25	0.25
53S-W	33,000	20,000	22.0	65	0.7	....	1.25	0.25
53S-T	39,000	33,000	14.0	80	0.7	....	1.25	0.25

*Per Cent Alloying Elements. Aluminum and Normal Impurities Constitute Remainder.

is designated as "W" while that obtained by aging the quenched sheet at elevated temperatures is designated as "T".

The compositions and the properties of these alloys in the various tempers are given in Table II. The effect of cold working and heat treatment on the mechanical properties are readily apparent from these data.

The temper of the original sheet required for items made from the common alloys depends on the severity of the draw. For severe draws, the annealed sheet is used while for less severe draws half hard or even the full hard sheet may be used.

In case of the 53S alloy, the part is generally drawn from the annealed (O) or the quenched (W) temper. The shell is then heat treated in such a way as to obtain the fully heat treated temper. In case of the shells drawn from sheet in the as-quenched or "W" temper, this means aging at 320 degrees Fahr. or slightly higher, the time at temperature depending on the temperature chosen. If drawn from sheet in the soft temper, quenching from 960 degrees Fahr. is required before the aging treatment. Whenever possible, the as-quenched or "W" temper is used because of the handling difficulty in heat treating the drawn shells as well as the distortion that occurs during the quenching operation. In most cases, this distortion is

sufficiently great to require corrective operations to bring the shell back to the desired shape.

Design of Draw Tools

The correct design of drawing tools is a very important factor in obtaining satisfactory shells. The general principles of design are the same as for other metals but the amount of reduction per draw, the radii on the tools, and the change in metal thickness will vary. These factors will be discussed under separate headings.

Reduction Per Draw—The reductions in diameter per draw for safe commercial production of 2S-O and 3S-O for deep drawn cylindrical shells are as follows:

Blank	D	Desired Reduction Per Cent	Permissible Per Cent
First Draw	(D_1)	40 (or less) D	42 D
Second Draw	(D_2)	20 D_1	25 D_1
Third Draw	(D_3)	15 D_2	18 D_2
Fourth Draw	(D_4)	15 D_3	15 D_3

These reductions may be varied to some extent but for sheet of commercial tolerance, trouble is usually encountered from fracturing of the metal if these reductions are exceeded.

For harder tempers of these alloys and for harder alloys such as 52S and 4S the reductions per draw have to be reduced. The increased hardness increases the resistance to flow of the metal to such an extent that fractures may occur when using the high reductions which are satisfactory for the annealed 2S and 3S sheet. In many cases, this decrease from the desired reductions given in the table may amount to 10 per cent on the first draw and 5 per cent on succeeding draws depending on the hardness of the metal being fabricated.

Radii on Draw Tools—The radius on the die should be approximately a minimum of 4T and a maximum of 15T where T is the thickness of the original metal while that on punch should be held to a minimum of 4T. The sharper the die radius the greater the resistance to the flow of metal. This resistance to metal flow is one cause of fracture during the drawing operations. On the other hand, if the radii are too large, a great portion of the metal in the blank is not under control while being drawn, and this may cause the formation of wrinkles. A liberal radius on the vertical corners of

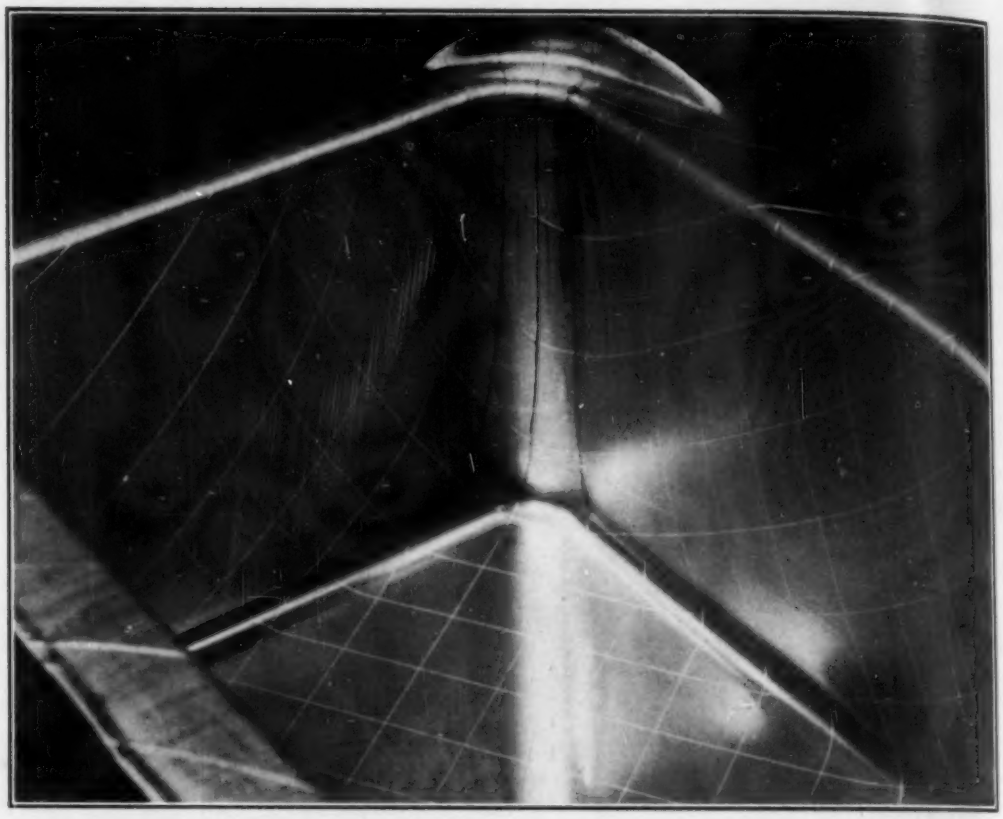


Fig. 1—Showing the Flow of Metal When Drawing a Rectangular Shell. The Great Change of the Square Sections in the Corner is Especially Noticeable.

rectangular shells is advisable as otherwise there will be too great a resistance to the flow of metal in this area.

Change in Thickness of Metal—The draw tools for aluminum should be designed so as to produce the minimum possible change in the thickness of the original blank. In many alloys, such as brass and steel, the reduction in cross section of the blank may be as high as 50 per cent of the original thickness. Such a forming procedure is usually not applicable to aluminum alloys. For this reason it is often necessary to redesign tools used for drawing other metals and alloys when it is desired to produce a similar shape from aluminum.

Shape to be Drawn

The shapes of drawn shells may be divided into four classes.

1. Rectangular
2. Cylindrical
3. Hemispherical
4. Odd Shapes.

The drawing of these will be discussed under separate headings.

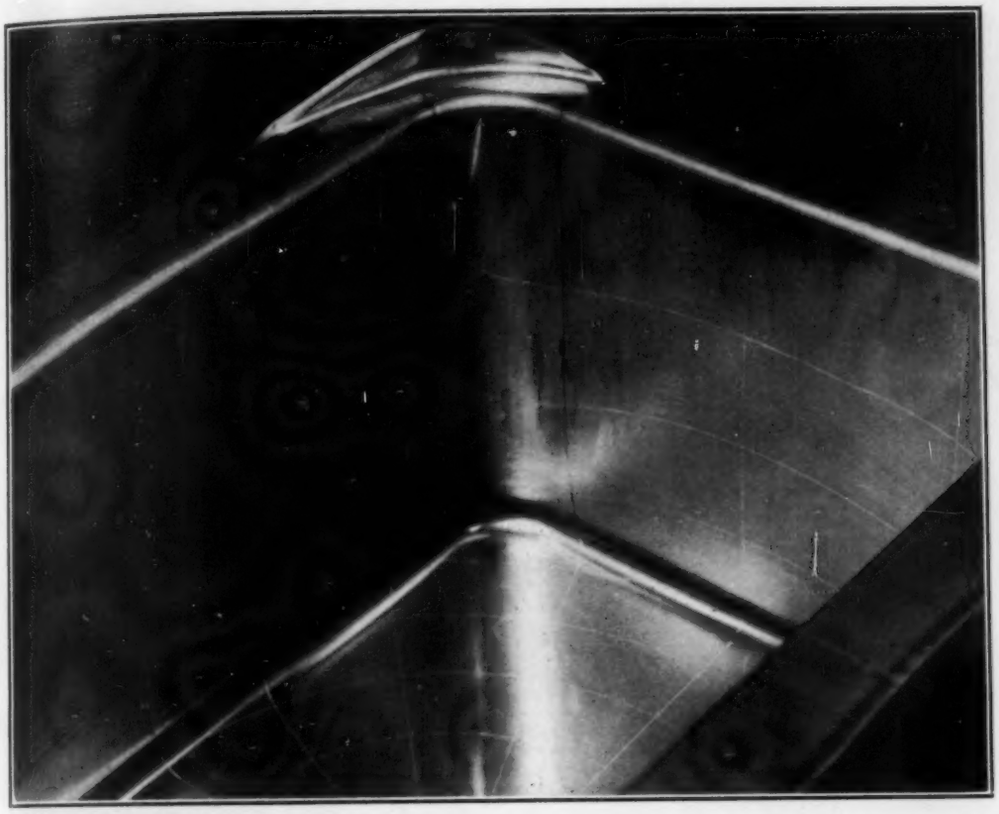


Fig. 2—The Flow of the Metal Is Shown by the Change in Position of Concentric Circles and Radial Lines. The Amount of Distortion in Various Parts of the Rectangular Pan is Readily Apparent.

Rectangular Shape—The flow of metal in drawing a rectangular shape is illustrated by the change in dimension of original squares as illustrated in Fig. 1, and the change in radial lines and concentric circles as illustrated in Fig. 2. These photographs show that the greatest movement of metal occurs at the corners. The die and blankholder must, therefore, be constructed to control this flow of metal so as to avoid both wrinkling and fracture.

This can be done by making the draw radius at the corners slightly longer than at the sides and ends, taking care to have the radii of different lengths blend smoothly into each other. Increasing the draw radius at the corners helps to reduce the resistance to flow caused by thickening of the metal. A procedure commonly used is to hollow out the face of the blankholder to provide the necessary clearance between the die face and blankholder to allow for this increase in thickness. This clearance should correspond nearly to the increase in thickness, because if it is too great, buckles extending radially from the corners will form in the drawing operation.

The dimensions of the original blank must be developed to obtain the proper amount of metal which is necessary to obtain the desired shell. The shape of the blank will vary greatly with the proportions of the rectangle and depth of shell to be drawn. A shallow rectangular pan or tray will require a blank of rectangular shape with the corners rounded. The blanks for a rectangular shell of medium depth will have only short, straight sides and ends with the

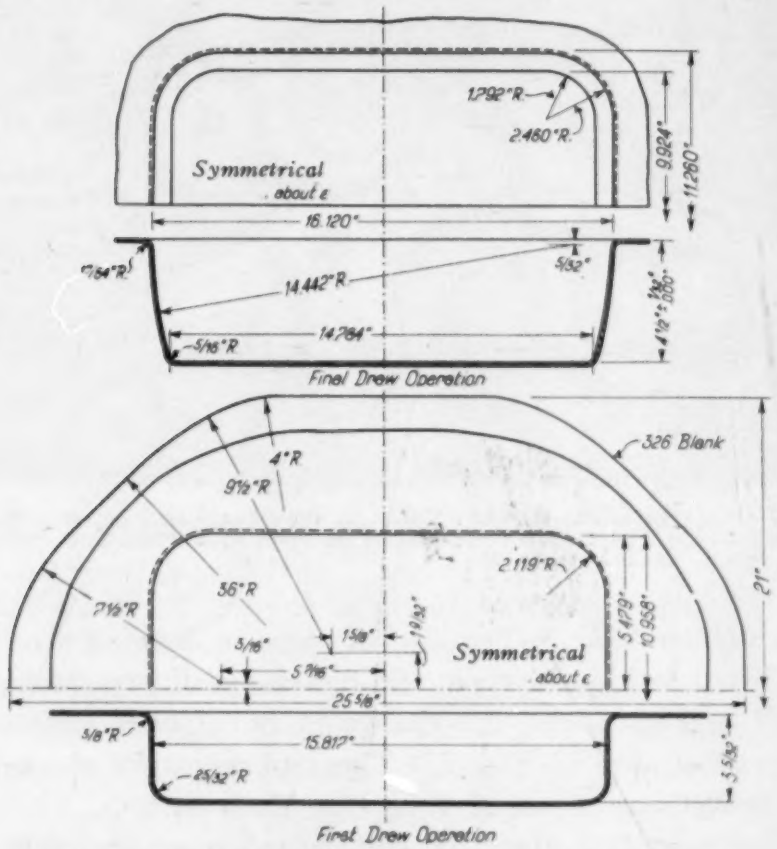


Fig. 3—Typical First and Second Operation Shells and Developed Blank for a Rectangular Pan.

corners cut away on a double ogee curve. Deep rectangular shells may be drawn from circular or elliptical blanks depending on the width to length proportion of the shell. Care should be exercised to use as little metal as possible in the blank as any excess metal increases drawing difficulties. Typical first and second operation shells, as well as the developed blank for a rectangular pan, are illustrated in Fig. 3. The die dimensions for the various draws are given in Table III.

Cylindrical Shape—The flow of metal in drawing cylindrical

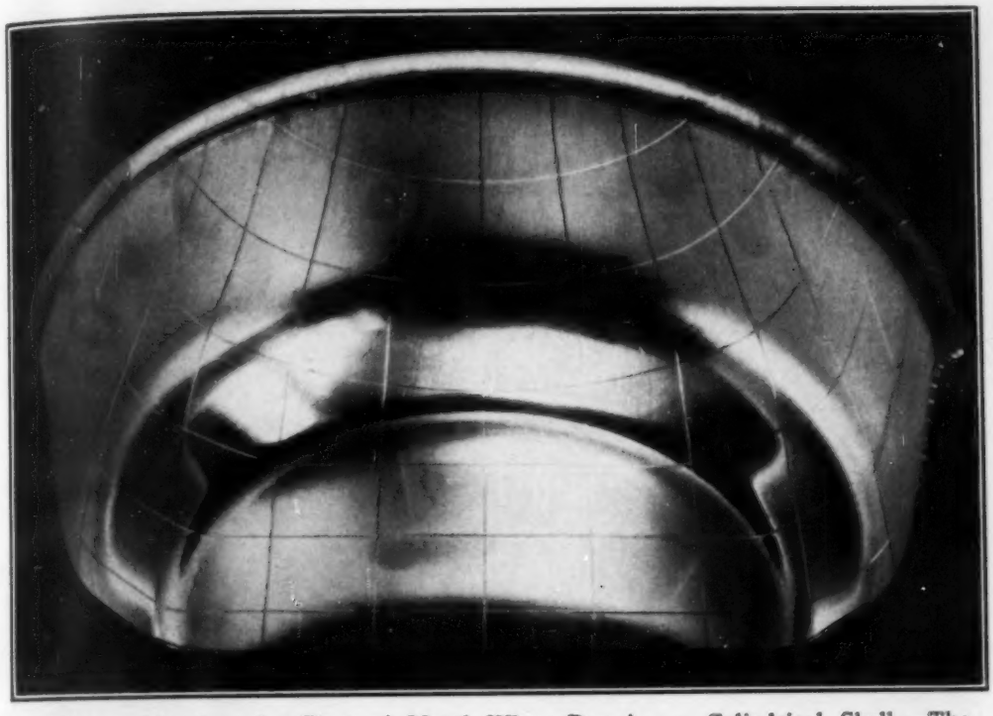


Fig. 4—Showing the Flow of Metal When Drawing a Cylindrical Shell. The Change in the Dimensions of the Squares Can Be Readily Seen.



Fig. 5—This is the Second Draw on the Shell Shown in Fig. 4. The Further Change in the Dimensions of the Squares is Apparent.

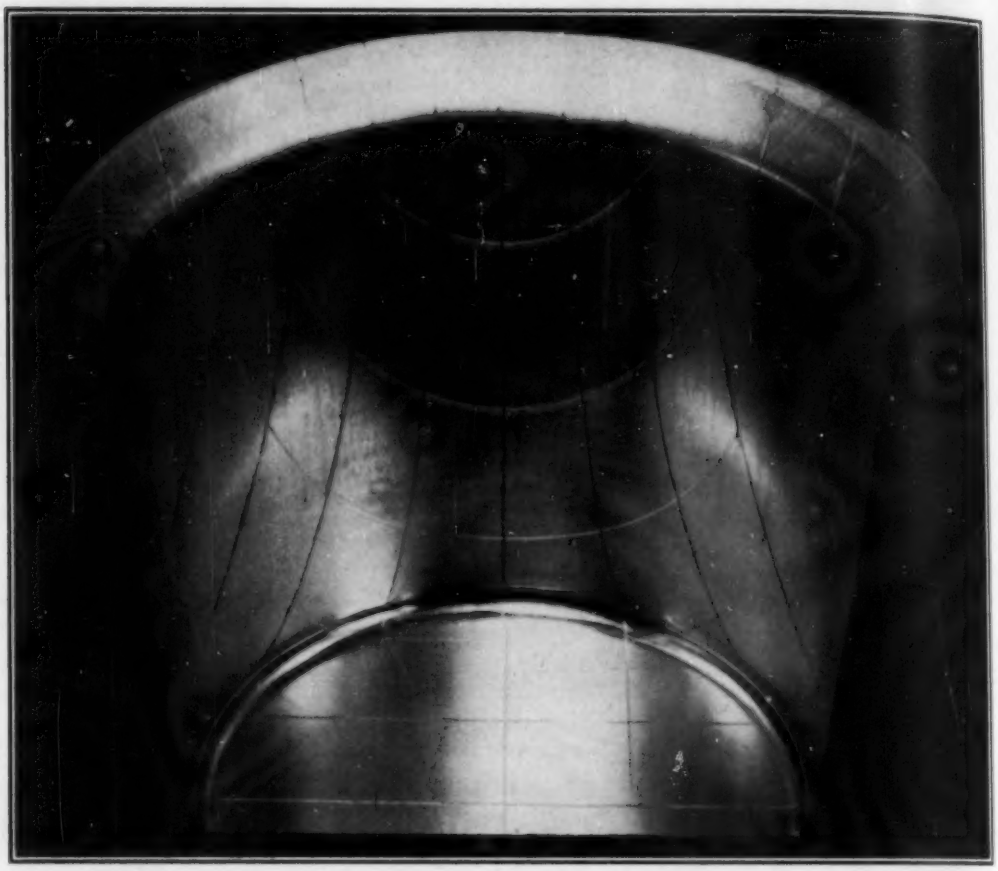


Fig. 6—This is the Third Operation on the Shells Shown in Figs. 4 and 5. The Original Squares in the Upper Part of the Shell Have Been Distorted to a Considerable Extent.

shapes is shown by the change in dimensions of squares as illustrated in Fig. 4 for the first draw, Fig. 5 for the second draw and Fig. 6 for the third draw. A careful check shows that even though the dimensions of the original square have been changed considerably, the area remains practically the same indicating little change in thickness of the metal during the drawing operation.

The sequence of drawing operations and the diameter of the original circular blank are given in Fig. 7. Since the metal moves the same in all parts of a symmetrical shape, no allowance has to be made in any particular part of the tool for thickening of the metal as was the case in rectangular shells. The die dimensions for various draws are given in Table IV.

Dome, Bowl and Hemispherical Shapes

The flow of metal in dome, bowl or hemispherical shapes is similar to that in cylindrical shapes. The dome or hemisphere is often difficult to obtain in drawing, especially with thin gage metal.

Table III

Die Dimensions for Various Drawing Operations of Rectangular Shapes

First Draw	Add 2.2 times blank thickness to Punch Dimension.
Second Draw	Add 2.2 times blank thickness to Punch Dimension.
Final Draw	Add 2 times blank thickness to Punch Dimension.

Table IV

Die Dimensions for Various Drawing Operations of Cylindrical Shapes

First Draw	Punch Diameter plus 2.2 times metal thickness of blank.
Second Draw	Punch Diameter plus 2.3 times metal thickness of blank.
Third and Succeeding Draws	Punch Diameter plus 2.4 times metal thickness of blank.
Final Draw of Tapered Shells	Punch Diameter plus 2 times metal thickness of blank.

because of the tendency to form wrinkles. In order to avoid difficulties in drawing such shapes, a preliminary draw is often required to obtain a sufficient amount of metal in the correct position before the final forming operation. If there is an excess of metal, wrinkling of the shell will take place while insufficient metal will cause fractures.

The procedure for drawing a bowl-shaped shell is illustrated in Fig. 8. The dimensions of the radii in the first drawing operation are very important as the shell must have sufficient metal at the proper positions so that the second draw can be performed without difficulty to produce the final shell.

The ratio of the inside diameter of drawn shell to the original metal thickness is very important when forming these hemispherical shapes in one draw and should be maintained below 200. A larger ratio usually causes difficulty because of wrinkles that form during the drawing operation.

Odd Shapes—Besides the shapes which have been discussed, various odd shapes are often desired. The flow of metal in such shapes may be a combination of those discussed. The sequence of operations for drawing a triplicate sauce pan as well as the original blank are illustrated in Fig. 9. Special attention should be given to the shape of the blank so as to use the least amount of metal to obtain the desired shape.

Materials for Drawing Tools

Various materials are used for making the drawing tools. The choice depends on the type of draw, the alloy sheet to be formed, the final finish on the drawn articles, the number of pieces to be fabricated as well as other conditions peculiar to individual plants.

Cast iron has been used to a considerable extent where the small number of pieces on an order makes it necessary to keep the tool cost at a minimum. The savings resulting from the use of cast iron is not only in the cost of material, but also in the cost of machining. Cast iron is also well adapted for draw tools when scratches obtained during drawing are not objectionable in finished items. The presence

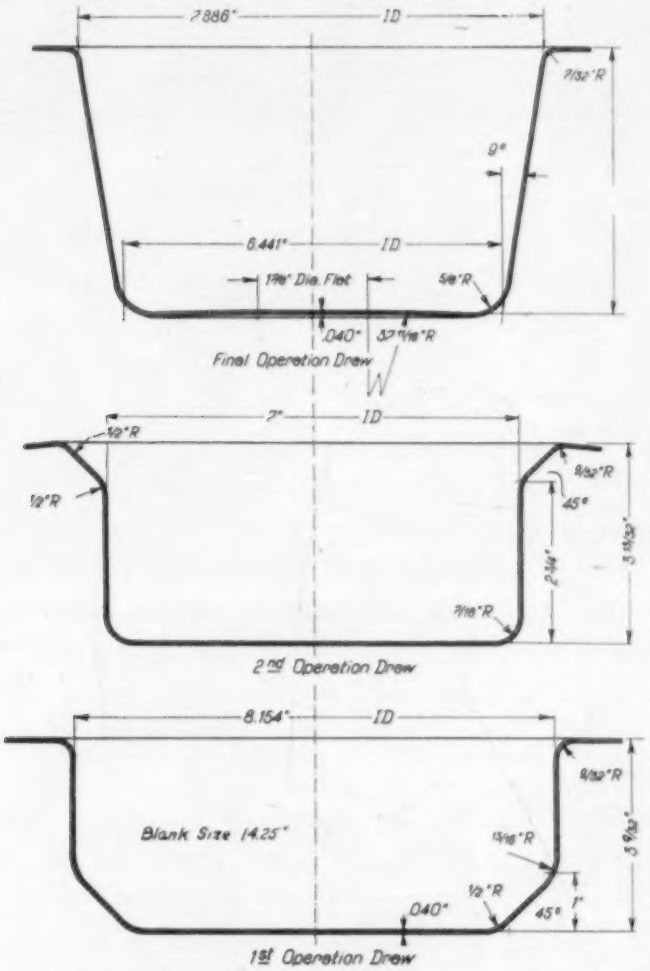


Fig. 7—Sequence of Drawing Operations and Diameter of Original Circular Blank.

of such scratches increases finishing costs if a highly polished surface is desired. At times, the increased finishing costs have to be balanced against the increased tool cost if made from steel to determine whether or not cast iron is more economical to use for the draw tools.

At the present time there are a number of grades of alloy cast iron which are superior to ordinary cast iron for draw tools. The

cost of these is somewhat higher, but this is often justified by the better results that are obtained.

The high grade alloy tool steels have been found to be the best for draw tools when the quantity of shells to be produced is sufficient to justify the cost. The stock is obtained as a forging so that more work has to be done to machine the tool than is the case with cast iron. The original cost of the steel is also considerably higher than

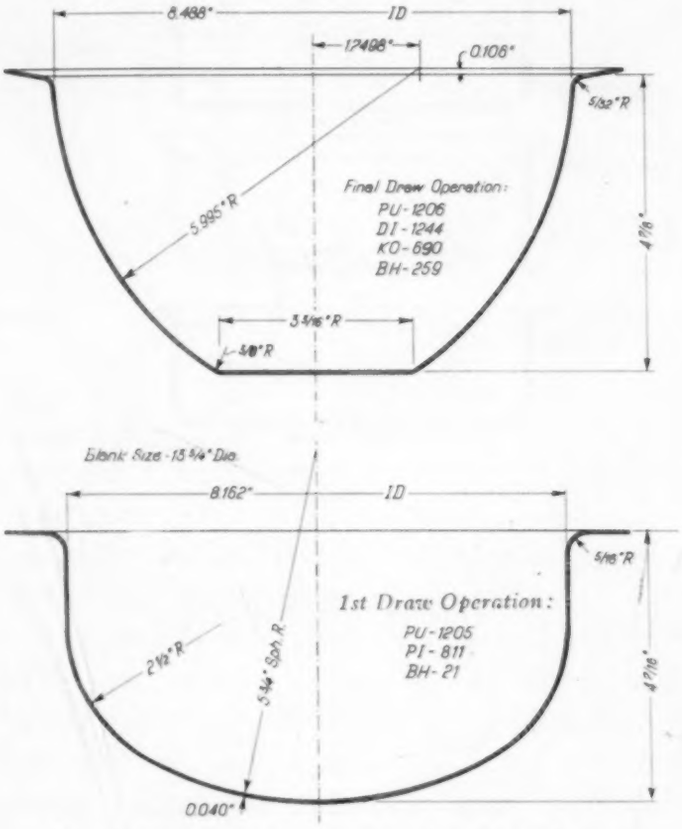


Fig. 8—Procedure for Drawing Bowl-Shaped Shell.

that of the cast iron. Oil hardening steels are usually used so that the maximum hardness with minimum distortion is obtained during heat treatment. Draw tools from the alloy steels are expensive and are used on large production runs, for drawing shells from hard alloys, and on items where scratches from the tools must be kept at a minimum.

Regular carbon steels containing 0.6 to 1.10 per cent carbon are intermediate in cost and performance between cast iron and alloy steels. They can be hardened by oil or water quenching from the upper critical and tempering to obtain the desired hardness.

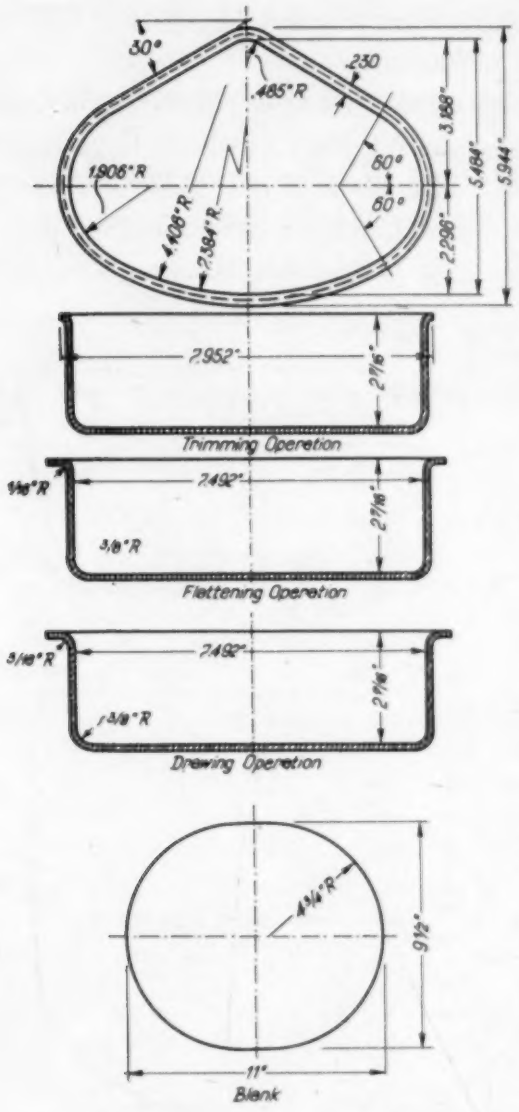


Fig. 9—Sequence of Operations for Drawing a Triplicate Sauce Pan.

Carburizing steels for draw tools are being investigated. The tests have not gone for a sufficient length of time to warrant definite conclusions. The indications are that they may be satisfactory for a number of applications where higher priced steels were formerly used.

Lubrication

The success or failure of many drawing operations depends on the proper selection of lubricants. Mineral oils or compounded mineral oils are the lubricants most commonly used for drawing alumi-

num. Water soluble drawing compounds have been tried, but results thus far indicate that some attack the aluminum if allowed to remain on it several days, while others do not have the desired lubricating qualities. The following table gives the types of oils that have been found satisfactory in plant operation. Others may be just as satisfactory so that the table should serve as a reference for selection of oils by comparison with those that have been found satisfactory.

Severity of Draw	Type of Lubricant
Light	Light Lubricating Oil
Medium	Mixture of Light Oil and Heavy Lubricating Oil
Severe	Heavy Lubricating Oil or 50% Mutton Tallow and 50% Paraffine Mixture
Very Severe	30% Mutton Tallow and 70% Paraffine Mixture

The lubricant performs two functions:

1. It allows the blank that is drawn to slip readily between the blankholder and die.

2. It provides the necessary lubrication to prevent scratching and galling while this movement takes place.

The proper choice of lubricant is a matter of experience and may vary in different plants for similar draws depending on the design of the tools, the material used for making the tools as well as the thickness of sheet drawn. Cast iron and low carbon steel tools require a heavier lubricant to prevent scratching than hardened steel tools. The greater the reduction per draw, and the sharper the radii, the heavier must be the lubricant to allow the blank to slip readily into the die. The thicker the sheet that is drawn, the heavier the lubricant that is required.

Operations subsequent to drawing may also influence the selection of lubricants. If the oil has to be removed by washing, either by hand or by machine, it is necessary for the lubricant to have the properties required at the draw, and also be readily removed by the cleaning procedure used in the plant in order that special cleaning practices shall not have to be adopted. A lubricant suitable for any one plant might be unsatisfactory in another, because it is difficult to remove in their cleaning operation.

Factors Which Affect the Drawing Quality of Sheet

The factors which affect the drawing quality of sheet are grain size, mechanical properties and earing tendency. These will be discussed under separate headings.

Grain Size—The microstructure of 3S alloy is shown in Fig. 10. It shows the network of grains in which are dispersed particles of the

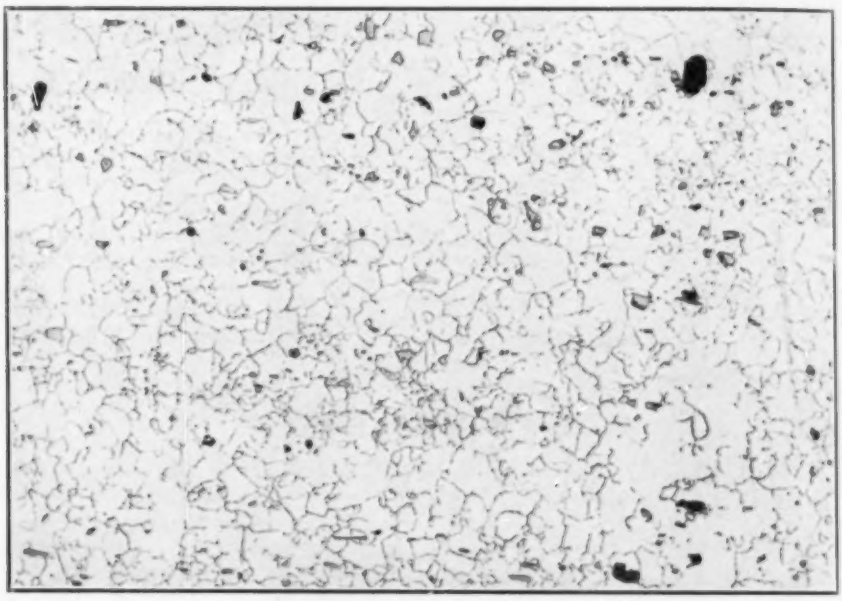


Fig. 10—Photomicrograph of 3SO Sheet. × 100.

manganese, iron and silicon constituents. Tests have shown that mechanical properties such as tensile and yield strengths and elongation are affected by the grain size. It is not surprising, therefore, that drawing properties are also affected by the size of grains.

No definite data has been obtained to show the effect of grain size on drawing properties. While in general, a fine grain is desirable, for some draws a medium coarse grain size has been found better than a very fine grain.

The Erichsen test has been used by some to indicate grain size and drawing characteristics. Our results to date have shown that this test does not give reliable results. The only satisfactory testing method has been to draw the metal into the desired shape and from this determine whether the metal has suitable drawing properties.

Mechanical Properties—The mechanical properties, tensile strength, yield strength, elongation and hardness have been suggested

Table V
Reductions in Die Setup for Drawing 3S0

		Per Cent
1.	Operation	43
2.	Operation	14
3.	Operation (Mainly Forming)	8

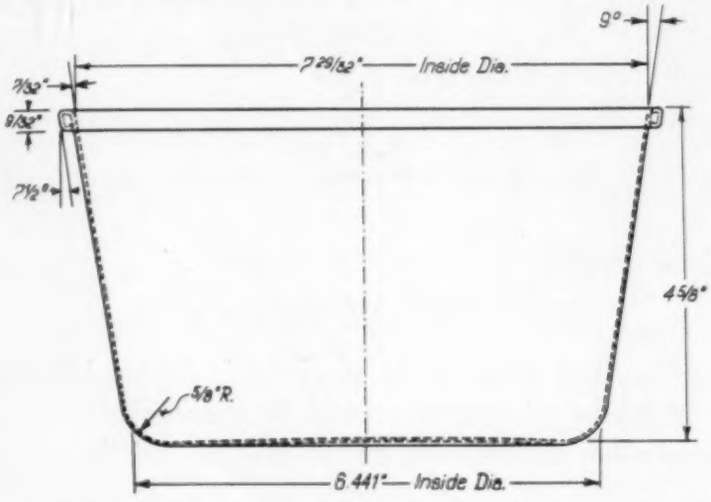


Fig. 11—Sketch of Pan Used in Studying the Effect of Mechanical Properties of Different Metals.

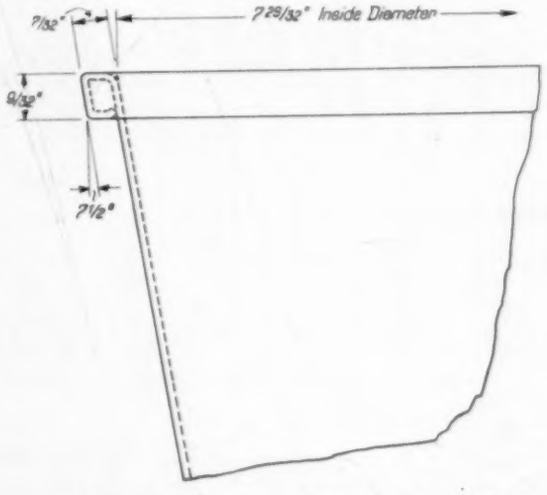


Fig. 11a—Enlarged View of Bend Section of Pan, Shown in Fig. 11.

as a test for indicating the drawing characteristics. It is usually assumed that the lower the yield strength, and higher the elongation, the better the drawing characteristics.

Our tests to date indicate that there is no definite relationship between mechanical properties and drawing characteristics. This is

not surprising when we consider the number of other factors that influence the drawing of metal.

In order to determine further the effect of mechanical properties, a pan illustrated in Fig. 11 was drawn using 3SO (annealed) 3S¼ Hard, 3S½ Hard and 3S Full Hard. The reductions per draw using 3SO are given in Table V. With this die setup the 3SO and 3S¼ Hard could be drawn into the shell without any breakage. All the other tempers broke in the first draw.

Table VI
Reductions in Die Setup for Drawing 3SH

		Per Cent
1.	Operation	30
2.	Operation	17.4
3.	Operation	14.0
4.	Operation (Mainly Forming)	8

A die setup was then made as given in Table VI. With these reductions, sheet in all tempers could be drawn into the pan. This test emphasizes the dependence of die design and the reductions per

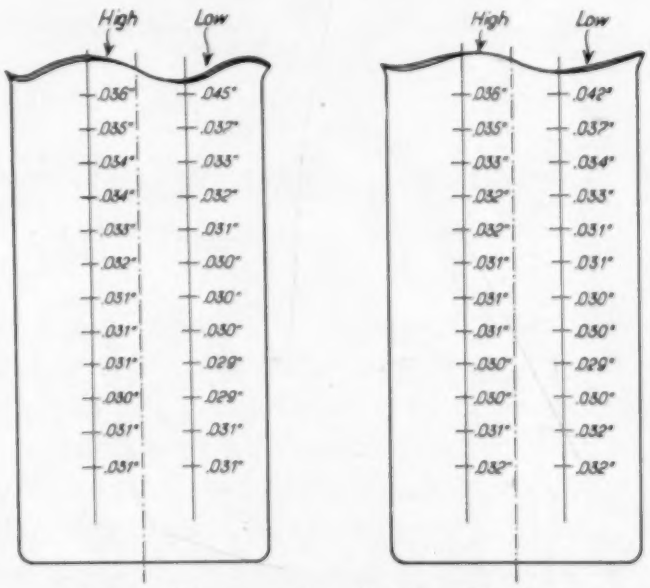


Fig. 12—Measurements Made on Shells Having Four Ears to Determine Whether There Was a Change in the Thickness of the Metal in These Shells.

draw on the drawing characteristics of sheet with varying mechanical properties.

Earing Tendency

The ideal drawn shell should have a uniform height or a uniform width of flange. In production it has been found that some shells

may have four or eight projections accompanied by a similar number of depressions. This condition is designated as "earing". The amount of earing may vary with different lots of metal or even within the same lot. It is desirable that the earing tendency be at a minimum because otherwise an excessive amount of metal has to be trimmed off to obtain a uniform height or flange. In some cases the original blank size based on metal that does not ear will not be large enough to obtain the desired height in the depressed areas.

Measurements were made on shells which had four ears to determine whether there was any change in the thickness of the metal in such shells. The results are given in Fig. 12. There is a decided thickening at the top of the shell in the low part as compared with the high part of the drawn shell. This may be caused by the variation in resistance to shear during drawing by grains having different orientations.

Table VII

Effect of Drawing on the Mechanical Properties of 3SO and 52SO

Alloy	No. of Draws	Thickness Inches	Tensile Strength	Per Cent Increase	Yield Strength	Elongation	Approx. Hardness
3S	0	0.103	16,000	....	6,000	30	O
	1	0.100	18,740	17.2	16,700	11.0	¼H
	2	0.097	22,140	38.4	20,800	9.0	½-¾H
	3	0.097	23,710	48.2	21,900	8.0	¾H
	4	0.098	24,240	51.5	22,300	7.5	¾H
52S	0	0.103	29,150	....	14,200	27.0	O
	1	0.101	34,390	18.0	31,600	6.0	¼-½H
	2	0.090	39,710	36.2	37,100	5.0	¾H
	3	0.087	42,680	46.5	38,600	5.5	H
	4	0.089	43,750	50.2	36,100	6.0	H

A number of factors such as composition of the alloy and rolling procedure affect the grain orientation in sheet. The shape of the shell to be drawn also influences the formation of ears as round shells show the effect of earing tendency much more than rectangular shells. This is very likely caused by the difference in the concentration of stresses in drawing.

Flow of Metal

The design of the dies and the adjustments of the blankholders during drawing should be such that the metal will take the desired shape without buckling and with minimum change in thickness.

Under these conditions the following stresses will be present during the drawing operation.

1. Compression
2. Tension
3. Shear.

Because the compression is most pronounced on the periphery of the blank, there should be a slight thickening of the metal towards the top of the drawn shell. This has been verified in measurements made on formed shells. In some draws, such as the forming of a dome shaped cover, considerable blankholder pressure is used which increases the tension on the metal. In such draws there may be a decrease in cross section.

Even though there is no great change in the thickness of metal when drawn into shells, there is a considerable amount of strain hardening resulting from cold work as indicated by mechanical properties of specimens taken from drawn shells. These properties during the various stages of drawing of 3SO and 52SO are given in Table VII. The small change in thickness is, no doubt, due to the movement by tension neutralizing that produced by compression which would cause a considerable amount of cold work without any appreciable change in dimensions.

In rectangular or odd shaped articles the flow of metal in various sections varies more than in round shells. Usually thickening occurs faster at the corners, and as previously stated, the design of the die must make allowance for this effect in order to avoid excessive blankholder pressure in this area which would cause the metal to fracture.

The change in properties of the metal in the drawn shell offers an explanation for the limits per draw previously listed. The first draw is made on a blank in the annealed (O) temper which allows a comparatively large reduction. Because of this draw the temper of the metal in the side walls is increased to approximately ¼H. On account of this increased hardness a lower reduction must be used in the second draw. The hardness of the metal in the side walls after the second draw is increased to approximately ½H so the third draw requires a smaller reduction. After this draw the hardness remains at ¾ to full hard so that the 15 per cent reduction is satisfactory for the fourth and succeeding draws.

From the results given in the table, it is noticed that while the percentage increase in tensile strength is about the same for both 3S and 52S, the actual increase in tensile strength is considerably

greater for the 52S. It has been found that the reductions per draw for alloys similar to 52S should be kept at the lower limits previously listed.

It should be remembered that the discussion of the flow of metal and the increase in hardness does not take into consideration drawn shells in which the cross section of the metal is changed appreciably. Such reductions are often made when forming cartridge cases or similar articles. In such draws other factors will affect the flow of metal which have not been taken into consideration in our paper.

The forming of metal in draw presses has been done for many years without receiving a great deal of attention in the literature. For this reason practices in different plants vary to a great extent and are usually the result of experience that has been gained over a period of years. It is believed that a great deal of useful information could be obtained by an exchange of ideas which would be of benefit to the metallurgists as well as the men in the plant. Such interchange of ideas is best obtained by presentation of papers before societies such as ours. It is hoped that others who are familiar with drawing of other metals and alloys will discuss this subject from their viewpoint which will lead to improvements that will benefit all those who are interested in this important subject.

DISCUSSION

Written Discussion: By E. V. Crane, E. W. Bliss Co., Brooklyn, N. Y.

The photographs accompanying this paper are extremely well prepared and make particularly valuable and excellent illustrations of the plastic flow which takes place in metal in drawing operations. The data accompanying the illustrations is thoroughly and completely recorded. It would be interesting, if in a future paper the authors would also correlate the change of physical properties during the drawing operation with the dimensions of the part and with the actual blankholding and drawing pressure for different reductions and heights of draw, which might possibly be obtained from the hydraulic drawing press mentioned in Table I. It would also be interesting if information were available on the maximum drawing velocity or crankpin velocity which has proven practical in the drawing of aluminum.

Authors' Reply

We appreciate the discussion by Mr. Crane. In answer to his question about speed of drawing, we have not found an upper limit in the speed of the ram using the present mechanisms of placing the blank on the die or getting the shell out of the press.

Further increase in the speed of the ram will be dependent on improvements in the blank feeding and shell removal mechanisms.

A HARDENABILITY TEST FOR SHALLOW HARDENING STEELS

By W. E. Jominy

Abstract

A method is presented for measuring the hardenability of shallow hardening steels using the end cooling principle. It has been found that steels having a hardenability of 1/4 inch or less on the standard bar now in use can be measured more accurately on the new bar. The test has been used on high, medium and low carbon steels and the results obtained are given in the paper.

THE method of measuring hardenability of steel by cooling one end of a bar and then measuring the length of the hardened zone has been used with good success for several years. This method was first described in 1937[1] as applying to carburizing steels and again in 1938[2] as applying to oil hardening steels. The method is especially suitable for alloy steels particularly those whose critical cooling rate is in the range between 5 and 150 degrees Fahr. per second. For shallow hardening steels, however, the method has not been so satisfactory because the drop in hardness comes very close to the water-cooled end of the bar due to the relatively high critical cooling rate of these shallow hardening steels.

The steels used in automotive applications which are usually given the most critical inspection are the alloy steels since these are commonly used where the stress concentration is high. These steels have occupied our attention for the most part and it was for these steels that the hardenability test was developed. However, we have recently had problems involving the hardenability of the more shallow hardening plain carbon steels and it was felt desirable to develop a test for these steels. It was also thought worthwhile to use the end cooling method and if possible the same equipment now used by a number of laboratories for the end cooling method of hardenability measurement.

After some experimentation a test was devised which appears

[1]American Society for Metals, Vol. 26, 1938, p. 574.
[2]Hardenability of Alloy Steels, American Society for Metals Publication, 1939, p. 66.

A paper presented before the Twenty-first Annual Convention of the Society held in Chicago, October 23 to 27, 1939. The author is associated with the metallurgical department, Research Laboratories Division, General Motors Corp., Detroit. Manuscript received June 23, 1939.

to fit the requirements just enumerated. It consists essentially of using our standard hardenability test bar which has had a tapered hole drilled in the water-cooled end and hardening on our regular test equipment. The test bar found to be most satisfactory is shown in Fig. 1. While many of the first tests were made on a bar 3 inches long, it was soon discovered that a 2-inch bar was long enough and

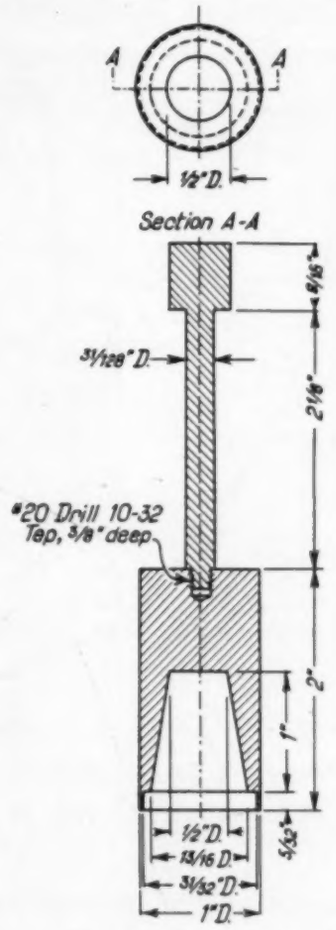


Fig. 1—Test Bar Design Found to be Most Satisfactory.

so the 2-inch bar was adopted for general use. In order to use this bar on the regular cooling equipment described last year, a longer adapter was necessary as shown in the figure. The important thing about this test bar is the shape of the hole cut in the end. This hole produces a wall thickness of $\frac{3}{32}$ inch at the extreme end to $\frac{1}{4}$ inch at the top of the hole. The test specimen is heated to whatever hardening temperature is desired, then hung vertically in the fixture on the hardenability equipment and water at 75 degrees Fahr. is

sprayed into the hole in the end. It has been our custom to increase the height of the water column to 4 inches before making a test with this type of bar whereas with our standard bar the height of the water column is kept at 2.5 inches. This is easily adjusted by means of the valve provided for the purpose in the standard equipment. The time of heating and the temperature used should correspond with that intended to be used in production operations. Likewise,

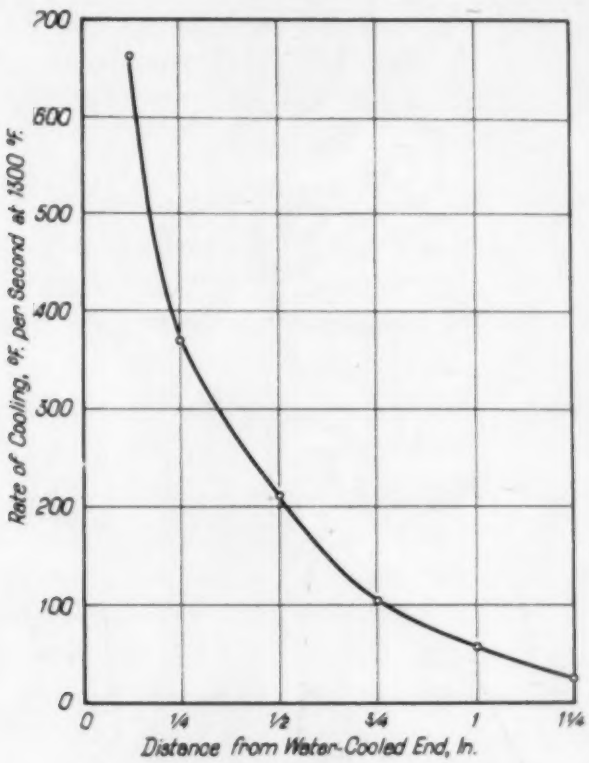


Fig. 2—Relationship of Location on Type L Bar and Cooling Rate.

the metallographic structure of the steel to be tested should correspond to what it will be in the production operation before hardening.

The type L specimen provides a gradual change in cooling rate along the bar so that shallow hardening steels may be graded for hardenability. In order to determine the cooling rate at various points on the bar a chromel-alumel thermocouple was welded to the surface of the bar at fixed distances from the end and the bar cooled on our standard fixture after heating to a proper temperature. The wires of the thermocouple were separately spot welded to the surface of the bar so that they were the same distance from the end and about ⅛ inch apart. Two or more cooling tests were made for each point investigated and the cooling rate at 1300 degrees Fahr. was

determined while the sample was cooled from 1700 degrees Fahr. on the standard fixture. A recording pyrometer was used to read the temperatures during the cooling cycle. The heating of the bars was done in a stainless steel container 2 inches in diameter and 7 inches high fitted with a cover $\frac{1}{32}$ inch larger in diameter than the container. Cast iron chips were placed in the bottom of this container to a depth of about 1 inch and the test specimen placed on these chips. With

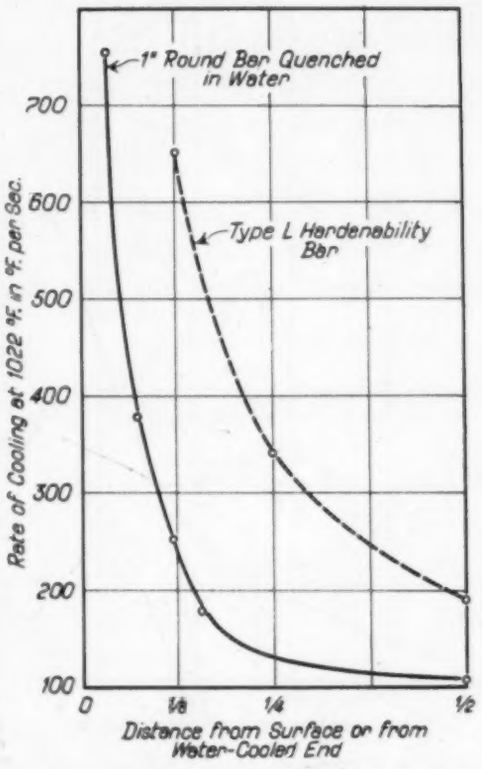


Fig. 3—Location of Equal Cooling Rates.

this procedure the specimen was kept nearly free from scale in the hole and with very little scale on the outside of the specimen.

The rate of cooling at the various points on the bar is shown in Fig. 2. The distances listed on the curve are measured from the bottom face and do not include the cupped part which extends $\frac{5}{32}$ inch farther. The rate of cooling was observed only to 1.25 inch from the bottom face as the rates beyond this are readily obtained on the standard bar. It has been especially gratifying to find the change in cooling rate quite gradual as compared to other bar shapes. For instance a 1-inch round bar quenched in water has a much more rapid change in cooling rate. According to Scott[3] a 1-inch round bar

[3]TRANSACTIONS, American Society for Metals, Vol. 22, 1934, p. 68.

quenched in water will cool at 1022 degrees Fahr. at the rate of 760 degrees Fahr. per second at 0.04 inch below the surface, at 378 degrees Fahr. per second at 0.08 inch below the surface, at 252 degrees Fahr. per second at 0.12 inch below the surface and at 180 degrees Fahr. per second at 0.16 inch below the surface. On our test bar for shallow hardening steel the cooling rate is 650 degrees Fahr. per second at 0.125 inch from the bottom, 340 degrees Fahr. per second at 0.25

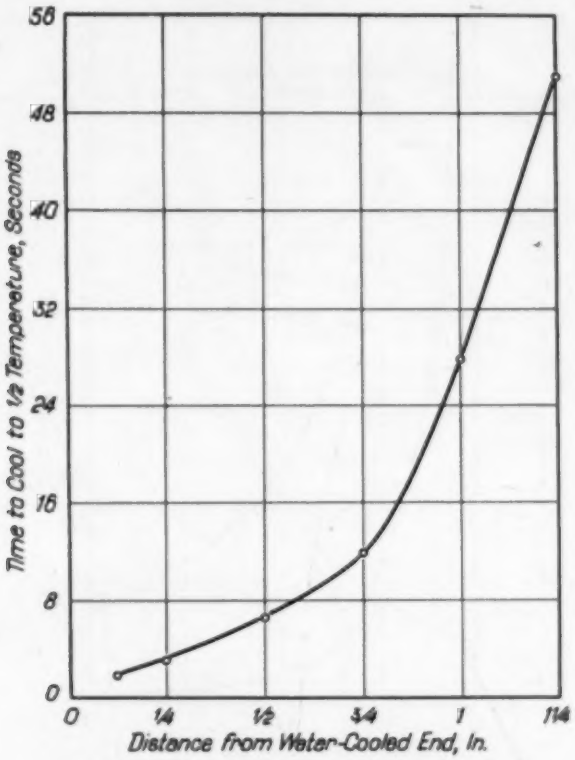


Fig. 4—Relationship of Location on Type L Bar and Time to Cool to ½ Temperature.

inch from the bottom, 245 degrees Fahr. per second at 0.375 inch from the bottom, and 190 degrees Fahr. per second at 0.50 inch from the bottom. The change in cooling rate is then about three times more gradual on our bar than on a 1-inch round quenched in water so that the test is more sensitive than with a 1-inch round bar. This is shown graphically in Fig. 3. In this figure is plotted the rate of cooling at 1022 degrees Fahr. at various distances from the surface of a 1-inch round bar quenched in water. This curve is replotted from Scott's[3] data. Using the same scale there is also plotted in Fig. 3 the rate of cooling at 1022 degrees Fahr. of various locations on the type L hardenability bar. A comparison may thus be had between the two bars. For instance a rate of cooling of 600 degrees

Fahr. per second may be found at $\frac{3}{64}$ inch beneath the surface of the water-quenched 1-inch round bar and at $\frac{9}{64}$ inch from the end on the type L hardenability bar. A change of rate of cooling from 600 to 200 degrees Fahr. per second corresponds to a distance of $\frac{3}{32}$ inch, from $\frac{3}{64}$ to $\frac{9}{64}$ inch beneath the surface on the 1-inch round water-quenched bar. On the type L hardenability bar the same change in rate of cooling corresponds to a distance of $\frac{11}{32}$ inch, from $\frac{9}{64}$ to $\frac{31}{64}$ inch from the water-cooled end.

Although cooling rate is usually considered when discussing hardenability, Grossmann, Asimow and Urban[4] prefer to consider what they call time to cool to one half temperature. That is the time required to cool from the bar temperature as the bar leaves the heating furnace to a temperature half way between the bar temperature and the temperature of the quenching medium. Fig. 4 shows the time to cool to one half temperature at the various points

Table I
Type L Bar Cooling Rate Data

Location Distance from Water Cooled End Inches	Average Cooling Rate at 1300 Degrees Fahr. °F./Sec.	Average Time to Half Temperature Seconds
⅛	665	1.90
¼	370	3.12
½	210	6.75
¾	115	12
1	54	27
1¼	26	51

on our shallow type bar. Table I shows the cooling rate as well as the time to cool to one half temperature at the various locations on the bar.

A number of steels have been tested for hardenability using this test bar. A series of steels containing in the neighborhood of 1 per cent carbon were among the first to be tested. These steels whose composition and grain size are listed in Table II were first tested by heating them in the form of our type L bar to 1450 degrees Fahr., the total time in the furnace being 30 minutes. It was found that the steels were all quite shallow hardening and when several tests for the same steel were compared, rather poor checks were obtained. It was decided that perhaps the time of heating was not long enough so the tests were again run using 1 hour's time. In this case all the duplicate bars of the steels checked well. Two tests were run on each of

[4]Hardenability of Alloy Steels, American Society for Metals Publication, 1939, p. 124.

the eight bars and the hardenability was rated by the distance from the bottom of the bar at which the hardness was Rockwell C 60 or more. The same result was obtained on each of the check tests with the exception of bars T-3. In this case one bar gave a result of $\frac{5}{16}$ inch and the other gave $\frac{9}{32}$ inch. It appears from these results that it is possible to obtain data which check within $\frac{1}{32}$ inch.

Table II
Composition and Grain Size of High Carbon Steels

Steel	Per Cent C	Mn	Cr	V	P	S	*Grain Size at 1500 Degrees Fahr.
T-1	1.12	0.28	0.13	....	0.005	0.012	6-8
T-2	0.96	0.33	0.19	....	0.004	0.011	7-8
T-3	1.01	0.30	....	....	0.008	0.013	2-3 and 6-8
T-4	1.08	0.37	0.41	0.17	0.005	0.012	7-8
T-5	1.20	0.38	....	....	0.006	0.015	7-8
T-6	1.11	0.37	0.15	....	0.005	0.014	7-8
T-7	1.01	0.22	trace	....	0.005	0.012	6-8
T-8	1.17	0.27	trace	....	0.006	0.012	5-8
T-9	1.05	0.31	0.56	0.16	0.007	0.010	6-8

*Determined by the oxidation method of Tobin and Kenyon. Heated 2½ hours at 1500 degrees Fahr.

These bars were again tested by heating to 1500 degrees Fahr. and cooling, also by heating to 1550 degrees Fahr. and cooling. The results of the test are given in Table III. The data obtained on four of these steels have been plotted in Figs. 5, 6, 7 and 8. It will be observed that the steels are all deeper hardening when cooled from 1500 degrees Fahr. than when cooled from 1450 degrees Fahr. Cooling from 1550 degrees Fahr. caused still deeper hardening to occur. This of course was expected.

Table III
Results of Hardenability Tests of High Carbon Steels

Steel	*Hardenability Cooled from 1450 Degrees Fahr.	Rate of Cooling °F./Sec.	*Hardenability Cooled from 1500 Degrees Fahr.	Rate of Cooling °F./Sec.	*Hardenability Cooled from 1550 Degrees Fahr.	Rate of Cooling °F./Sec.
T-1	$\frac{5}{16}$	310	$\frac{3}{8}$	270	$\frac{1}{2}$	210
T-2	$\frac{3}{8}$	270	$\frac{1}{2}$	210	$\frac{9}{16}$	....
T-3	$\frac{5}{16}$	310	$\frac{3}{8}$	270	$\frac{1}{2}$	210
T-4	$\frac{1}{2}$	210	$\frac{3}{4}$	115	$\frac{7}{8}$	80
T-5	$\frac{1}{2}$	210	$\frac{5}{8}$	155	$\frac{3}{4}$	115
T-6	$\frac{1}{2}$	210	$\frac{3}{4}$	115	$\frac{3}{4}$	115
T-7	$\frac{1}{4}$	370	$\frac{3}{8}$	270	$\frac{3}{8}$	270
T-8	$\frac{1}{4}$	370	$\frac{3}{8}$	270	$\frac{3}{8}$	270

*Distance in inches from bottom of specimen where hardness was Rockwell C 60 or more.

In Table III are also shown the cooling rate in degrees Fahr. per second necessary to get a hardness of Rockwell C 60. It may

be seen from the table that at 1450 degrees Fahr. the cooling rate necessary to get a hardness of C 60 on these steels is 370 degrees Fahr. per second on the shallowest hardening steel to 210 degrees Fahr. per second for the deepest hardening steel. When cooled from 1550 degrees Fahr. these steels differ more in hardenability than

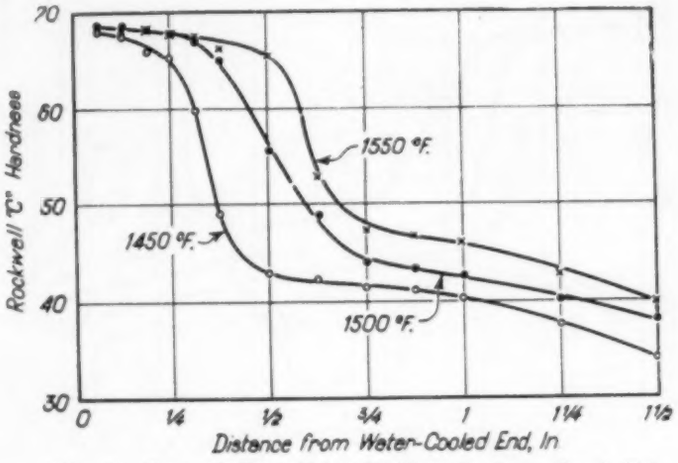


Fig. 5—Type L Bar Hardenability Curves. Steel T-1.

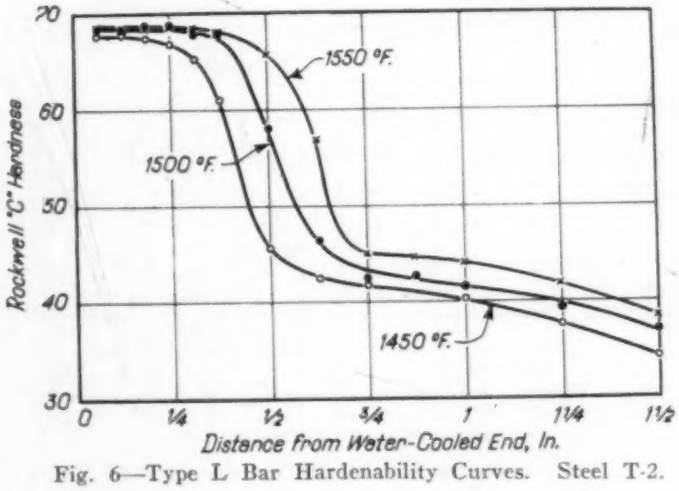


Fig. 6—Type L Bar Hardenability Curves. Steel T-2.

when cooled from 1450 degrees Fahr. Here the cooling rate necessary to produce a hardness of Rockwell C 60 varies from 270 degrees Fahr. per second for the shallowest hardening steel to 80 degrees Fahr. per second for the deepest hardening steel.

Fig. 9 shows the hardenability curves of steel T-9 after heating for ½ hour, 1 hour, and 2 hours at 1450 degrees Fahr. and cooling on the standard fixture. As will be observed there is only a small difference between the curve corresponding to a heating time of 2

hours and that for 1 hour. There is however a large difference in hardenability between the heating time of 1 hour and that of ½ hour. Considering the usual rule of allowing 1 hour per inch of thickness, ½ hour should be long enough to heat the section at the ¼-inch point but it appears to have been quite insufficient. While

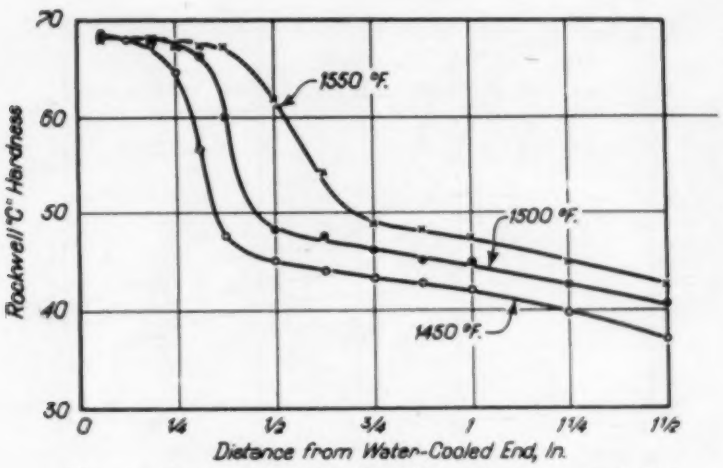


Fig. 7—Type L Bar Hardenability Curves. Steel T-3.

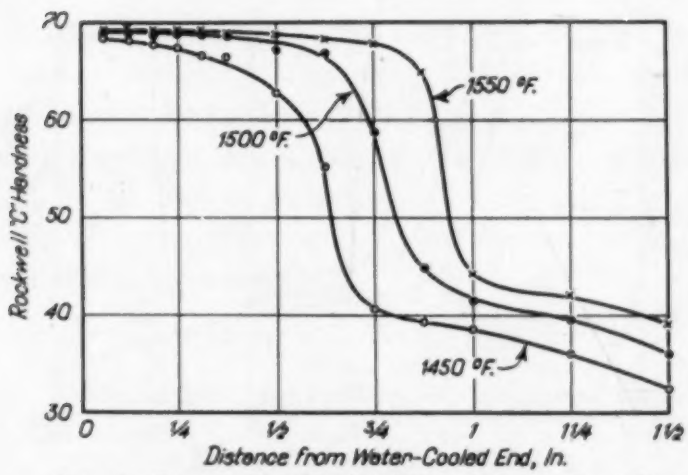


Fig. 8—Type L Bar Hardenability Curves. Steel T-4.

it is true that this steel had its carbide in the spheroidal form, it is also true that most commercial steels containing 1 per cent carbon are supplied in the spheroidized condition.

A metallographic examination was made of two of the hardenability bars—the bar heated ½ hour and the one heated 1 hour. The sections were taken at $\frac{5}{16}$ inch from the water-cooled end in both cases and are shown in Figs. 10 and 11. The hardness on the bar heated ½ hour at this point was Rockwell C 42 and on the bar

heated 1 hour was Rockwell C 66. The photomicrograph of the steel heated 30 minutes shows free ferrite areas whereas the bar heated 1 hour shows none. This appears to be plainly a case of insufficient time for complete solution.

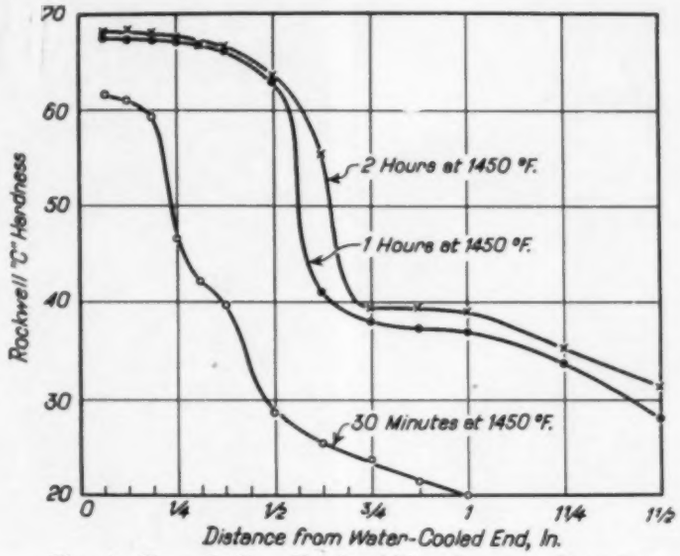


Fig. 9—Type L Bar Hardenability Curves. Steel T-9.

Fig. 12 shows the structure of the bar which was heated 1 hour at a point 1.25 inch from the water-cooled end where the hardness was Rockwell C 33. As may be seen, no free ferrite is present even with the slow rate of cooling at this point.

Table IV
Composition and Grain Size of Low and Medium Carbon Steels

Steel S.A.E. No.	Per Cent C	Mn	Ni	Cr	Mo	V	S	Grain Size
1020	0.19	0.49	....	....	....	.....	0.031	6–7
1050	0.50	0.70	....	....	....	.....	.....	5–6
2315	0.18	0.67	3.63	....	....	.....	0.019	3–4
3115	0.14	0.50	1.08	0.68	....	.....	0.029	6
4615	0.19	0.52	1.88	....	0.27	.....	0.017	6–8
4815	0.15	0.49	3.56	....	0.23	.....	0.014	6–7
5115	0.14	0.70	....	0.94	....	.....	0.025	6
6115	0.19	0.48	....	1.23	....	0.017	.....	6–7

The phosphorus in all these steels was under 0.025 per cent.

A number of medium and low carbon steels have been tested with the type L bar. Some of these steels are listed in Table IV which gives their composition and grain size. The S.A.E. 1050 steel was cooled from 1550 degrees Fahr. and the other steels were cooled from 1700 degrees Fahr. The time of heating for these steels was

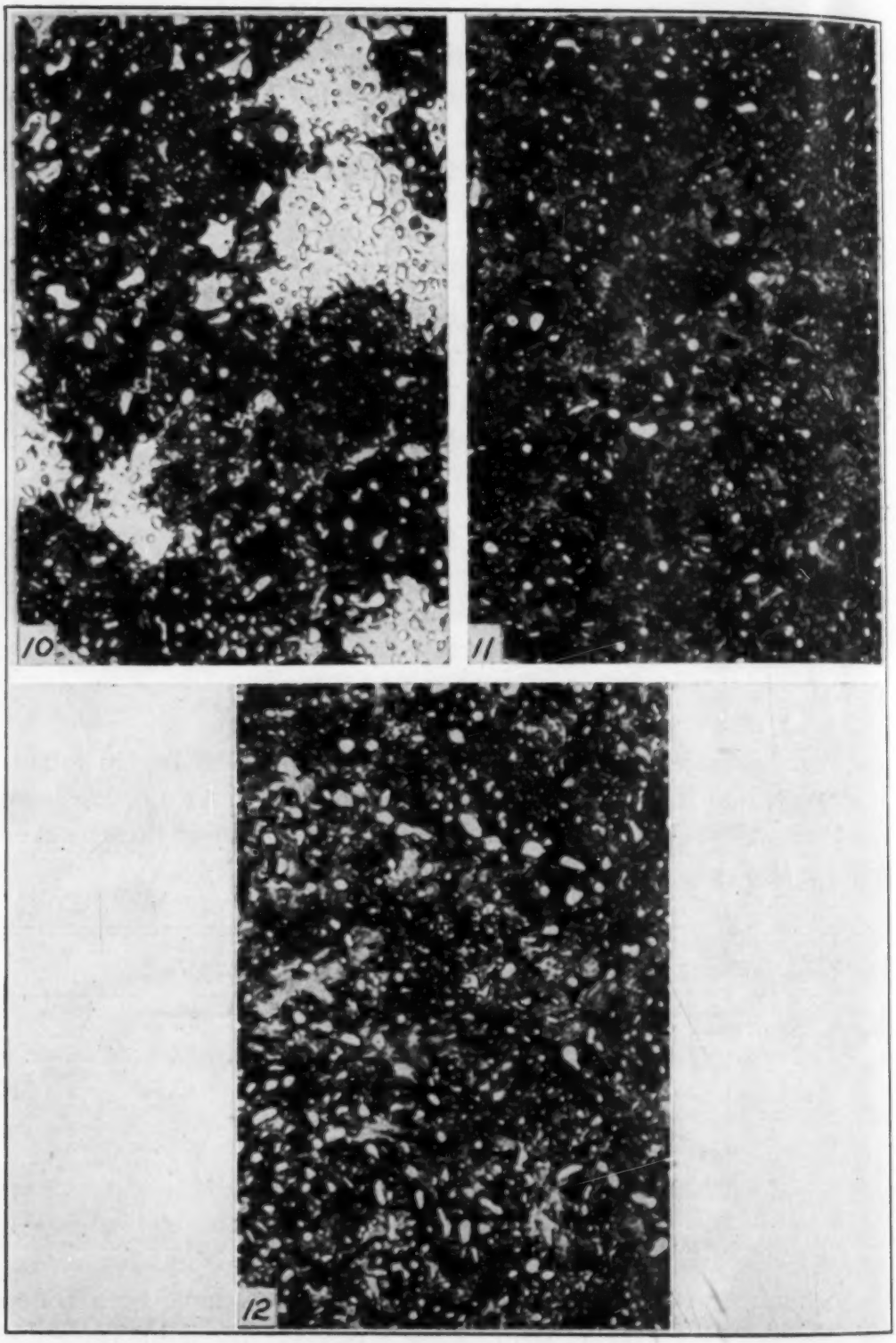


Fig. 10—Photomicrograph of T-9 Steel at $\frac{1}{16}$ Inch Position on Hardenability Bar. Heated 30 Minutes. Etched in Nital. × 1000.

Fig. 11—Photomicrograph of T-9 Steel Same Location as Fig. 11. Heated 1 Hour. Etched in Nital. × 1000.

Fig. 12—Photomicrograph of T-9 Steel at 1¼ Inches Position on Hardenability Bar. Heated 1 Hour. Etched in Nital. × 1000.

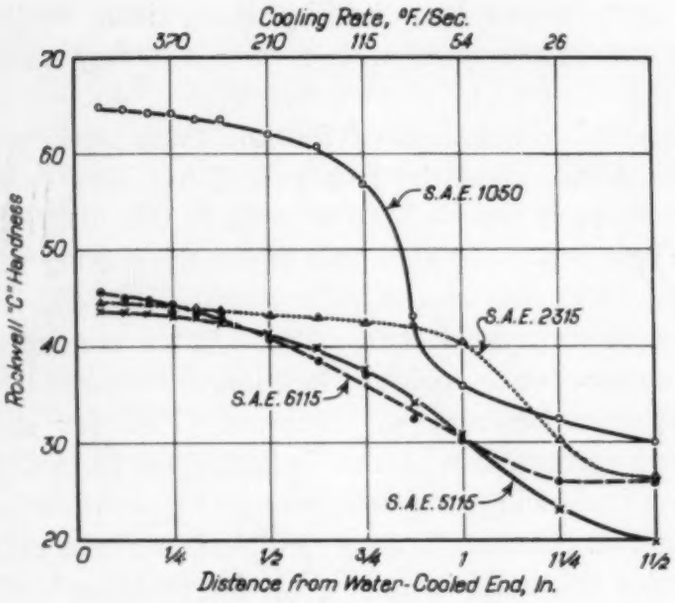


Fig. 13—Hardenability Curves Type L Bar. S.A.E. Steels as Shown.

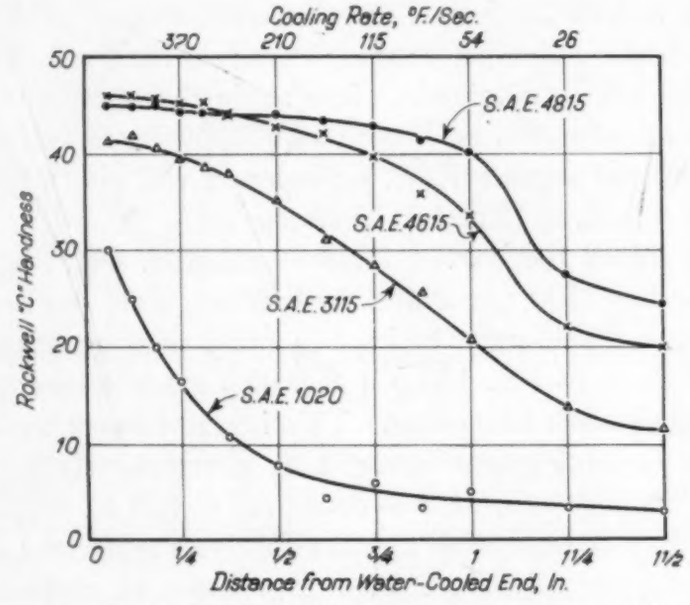


Fig. 14—Hardenability Curves Type L Bar. S.A.E. Steels as Shown.

30 minutes. Several of the steels could be measured as well on our standard bar and would not need to be tested with the type L bar. Such steels as the S.A.E. 2315 and 4815 could easily be measured on our standard bar. These steels have been presented, however, to give a comparison with shallow hardening steels and to show that the type L bar is suitable for relatively deep hardening steels. It has been

found that steels whose hardenability is ¼ inch or less on the standard bar can be measured with greater accuracy on the type L bar.

The hardenability readings of four of these steels are given in Fig. 13. This figure gives the Rockwell C hardness corresponding to the locations on our type L bar for steels S.A.E. 1050, 2315, 6115, and 5115. There is also listed in this figure the cooling rate at 1300 degrees Fahr. which has been obtained at ¼, ½, ¾, 1, and 1¼-inch locations on the type L bar. These latter are not exactly to scale but are correct for the point of location.

The maximum hardness of Rockwell C 65 for steel S.A.E. 1050 is in good agreement with that indicated on Burns, Moore and Archer's[5] curve showing the maximum hardness obtainable for steels of all carbon contents from zero to 1.00 per cent carbon. The hardenability for this steel is quite good for plain carbon and from the curve it appears that with a cooling rate of 210 degrees Fahr. per second the hardness will be Rockwell C 60 or above.

For the S.A.E. 2315 steel the curve shows that with a cooling rate of 54 degrees Fahr. per second or more a hardness of Rockwell C 40 to C 45 will be obtained. Here again the maximum hardness obtained agrees with Burns, Moore and Archer's curve. The same rate of cooling (54 degrees Fahr. per second) will give a hardness of C 30 for the S.A.E. 6115 and 5115 steels.

Fig. 14 shows the curves for steels S.A.E. 4815, 4615, 3115, and 1020. It should be noted that the ordinate scale has been shifted on this curve and this must be kept in mind in comparing steels in Fig. 14 with those in Fig. 13. Of the alloy steels tested the S.A.E. 3115 is the shallowest hardening. This is due in part we believe to its relatively low manganese content as compared to S.A.E. 5115 steel and its low carbon content as compared to S.A.E. 4615 and 6115 steels. The S.A.E. 4815 steel appears to give the deepest hardening characteristics especially since its manganese and carbon contents are as low as those in the S.A.E. 3115 steel. The S.A.E. 1020 steel is decidedly the shallowest hardening steel of all and is in a class by itself in this regard. Since Rockwell C readings are not considered accurate below C 17, the points on the curve below this value are only approximate and are presented merely to give comparative values with the other steels.

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[5]Hardenability of Alloy Steels, American Society for Metals Publication, 1939, p. 124, and TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 1.

In addition to testing the steel, this data may be used to estimate the behavior of steel when machined into parts and heat treated. For example, the Chevrolet rear axle drive pinion has been found to cool at the rate of 55 degrees Fahr. per second at 1300 degrees Fahr. when quenched in strongly agitated oil from 1700 degrees Fahr. at a point corresponding to the center of a gear tooth at the base. If this pinion were made from any of the steels listed on the curves and were carburized and quenched directly from the carburizing temperature into oil, we can determine what hardness would be obtained at the center of the gear tooth at the base. If made from S.A.E. 1020 steel, the hardness would be less than Rockwell C 10; if made from the S.A.E. 3115 steel shown in Fig. 11, the hardness would be Rockwell C 21; if made from the S.A.E. 5115 or 6115 steels, the hardness would be Rockwell C 30; if made from the S.A.E. 4615 steel, the hardness would be Rockwell C 33; and if made from the S.A.E 2315 or 4815 steels, the hardness would be Rockwell C 40. It should be remembered that steels having a carbon range of 0.10 to 0.20 per cent will vary considerably in hardness though they be of the same type, so that in studying such steels due allowance must be given to the actual carbon content.

The author is indebted to Mr. A. L. Boegehold for his many helpful suggestions and to Mr. Eric Weinman who made most of the tests.

DISCUSSION

Written Discussion: By O. W. McMullan, Youngstown Sheet & Tube Co., Indiana Harbor Works, E. Chicago, Ind.

The use of a specimen which extends the zone of hardness drop in end quenching tests is a desirable addition to the method when testing shallow hardening steels. The type L specimen, however, is one which machinists object to making unless lathe equipment is new and even then it is not a simple job. In regard to using the same equipment now in use in various laboratories it might be remarked that different equipment is being made for the skirted and beveled end specimens and the two are not interchangeable. The equipment the writer uses was not designed to handle a skirted specimen like type L and changing to a bevel might affect results near the thin end. Presumably the author did not find a specimen of simpler design, such as a smaller cylinder beveled at the end, to be suitable. Interchangeable conical seats of different diameter would not have greatly complicated the design of the quenching fixture.

Fig. 9 shows that increasing the time of holding at temperature before quenching is similar in effect to increasing the temperature from 1450 to 1550

degrees Fahr. and using a constant holding temperature as shown by Figs. 5 to 8. Holding time at 1550 degrees Fahr. to produce maximum depth hardness would probably be less than the required holding time at 1450 degrees Fahr. The effect appears to be the result of a time-temperature relationship necessary to get the carbides into solution rather than only the temperature from which cooling is started. Perhaps the statement on page 1078 that it was expected that all the steels would be deeper hardening when cooled from increasingly higher temperatures between 1450 and 1550 degrees Fahr. could be amplified in this respect. Would this be true if the steel were of such composition (previous microstructure also having an effect on required time at temperature) that all carbides would dissolve at 1450 degrees Fahr.? Another angle of approach would be by heating to higher temperatures and then equalizing at 1550 and 1450 degrees Fahr. before quenching. This subject of delayed quenching has been a source of considerable variation in opinion and the end quenching method should offer a good means of determining the effect of the method on depth hardness.

The author's data on cooling rates at 1300 degrees Fahr. of different points along the specimen were determined on specimens cooled from 1700 degrees Fahr. In Table III those data have been applied when cooling started at 1450, 1500, and 1550 degrees Fahr. Is it strictly true that cooling rates at 1300 degrees Fahr. of various points on the specimen would be the same regardless of temperature from which cooling started?

Written Discussion: By Gordon T. Williams, metallurgist, testing and research laboratory, Deere & Co., Moline, Ill.

The specimen for shallow hardening steels is especially interesting to the discusser because of his own tests, described in another paper, which showed that varying water temperature, or length or diameter of the flat-end hardenability specimen did not change the resulting hardness curve, and it was obvious that a modified shape would have to be used to increase the possible number of hardness test points through the portions showing greatest change in cooling rate. Mr. Jominy has provided a design which does this excellently, although the specimen is by no means easy to make.

The cooling rates for the new bar are not the same as found by Jominy on the flat-end bar for given distances from the quench face; for example, at ½ inch along the type L specimen, the quenched face is $\frac{1}{8}\frac{1}{4}$ inch away, and a cooling rate at 1300 degrees of 210 degrees per second is given; at $\frac{1}{8}\frac{1}{4}$ inch along the standard bar he found a rate of about 100 degrees per second. Such differences are perhaps due to the added effect of the flat inner end of the taper hole.

Can the author give any data regarding effect of a change in steel type on cooling rates? It might be expected that the change in recalescence with varying analysis might affect the cooling rate considerably. We have noted that steels appeared to differ greatly in the overall total cooling time. For that reason it would seem safer to compare similar steels only, in translating test bar values to expected results in finished sections.

It might be of interest to note that the cooling rates in a 1-inch round cited from Scott's work and the cooling rates previously given by Mr. Jominy (TRANSACTIONS, American Society for Metals, Vol. XXVI, p. 582) for vari-

ous distances from the quenched end will fall on the same curve when plotted; in other words, up to ½ inch from the quenched end, the standard hardenability curve should coincide with the traverse of a 1-inch round.

The writer has employed a useful variation of the standard test, for carburized steels; readings are taken along the surface or at a selected small depth below the surface of the hardened specimen; a surface is then ground flat below the case, and core hardening curve is obtained. It might also be mentioned that the effect of the case in reducing core hardening is found by this test just as by traverses, and hence the core hardenability should be determined with the case present.

Written Discussion: By H. W. McQuaid, assistant chief metallurgist, Republic Steel Corp., Cleveland.

The end-quench test, as described by Messrs. Jominy and Boegehold at the 1937 Annual Meeting, furnished a long needed test for hardenability, which promises to eliminate all others as a means for the evaluating of hardenability of alloy steels. The valuable quality of this test was that it was independent of size or length of specimen, and gave in one test practically complete information as to the comparative hardenability of the steel being tested in any section or quenching medium. It was based on the fact that the cooling rate of any point in a piece of steel was the same as any other point which was the same distance from a surface maintained at constant temperature. In the Jominy end-quench test piece the end of the specimen is maintained at a temperature of approximately 70 degrees and theoretically this is the only important factor for the rate of cooling of a point at a given distance from the cold end.

The test piece described in the present paper, while ingenious and useful, falls into the class of an arbitrary test piece which is no longer independent of diameter or length. There is no doubt in my mind but what it is extremely practical and overcomes the objection of the end-quench Jominy test in that it magnifies variations in hardenability in steels of the shallow hardening type. It will be used to supplement the end-quench Jominy type but will probably require considerable investigation before it could be accepted as a standard test on carbon steels.

It is of interest that Mr. Jominy found difficulty in obtaining uniform hardenability unless he increased the quenching temperature to obtain more complete carbon solution and diffusion. It is my opinion that much of the difference in hardenability which has been ascribed to variation in the size of the austenite grain is due to a nonhomogeneous distribution of the carbon in the austenite. Apparently we have more difficulty in some heats than in others in obtaining uniform carbon diffusion, so that, at the time of quenching, there are boundaries and perhaps other areas low in carbon which have a high transformation rate. When this occurs the hardenability is relatively low.

Oral Reply

A. L. BOEGEHOLD:[6] I am not going to cover all of the points that were brought up by the discussers. I think I will leave that for Mr. Jominy, but I might make a few remarks on the type specimen. We have not found that

[6]Research Laboratories Division, General Motors Corp., Detroit. Mr. Boegehold presented the Jominy paper in his absence.

machining this type specimen causes any difficulty. You will be satisfied it is not too difficult when you get used to making it.

Concerning the interchangeability with a standard specimen, I might say that we have discontinued using the beveled seat for the plain ended specimen. It is only necessary to hang the specimen in the spot provided for the skirted end specimen and direct the stream of water at the bottom of the specimen and no water goes up the side of the specimen. So you can throw away your fixture with the beveled seat making one quenching apparatus suitable for all types of specimens.

The determination of cooling curves starting from an initial temperature of 1700 degrees Fahr. and from 1450 degrees Fahr. have been made on a standard hardenability specimen, but has not been made on the type L specimen. We found that whether you started at 1700 or 1450 degrees Fahr., the cooling curves were almost identical and we have assumed that the same is true for the type L specimen. This point however will require checking.

The point that Mr. Williams brought up about high carbon steels and low carbon steels is pertinent, because high carbon steels, having a lower thermal conductivity, do cool slower, and it is going to be necessary to make cooling rate curves on the two types of steels in order to get the most accurate results.

That has not been done yet but it is on the docket for doing later on.

Author's Reply

Mr. Boegehold answered some of the questions raised by Mr. McMullan in his verbal reply to the discussion. We have not found any measurable difference between the results obtained with the type L bar whether hardened on either of the two types of hardenability machines now in use. I agree with Mr. McMullan that a time-temperature relationship is involved in the development of hardenability. The relative completeness of carbide solution and grain size of a steel of given composition appear to be the important factors affecting hardenability. Mr. Williams has introduced an additional factor of diffusion. Heating to a higher temperature than 1450 degrees Fahr. and then cooling to 1450 degrees Fahr. would probably reduce the necessary time of heating but would be expected to produce the grain size of the higher temperature.

Mr. Gordon Williams brings up the question of change in steel type affecting the cooling rates. In our standard test we keep a record of the time required to cool the specimen to about 120 degrees Fahr. or the temperature where we can just endure holding our fingers at the top of the bar. We have found that about 13 or 14 minutes is required for steels of medium hardenability. However, for steels having deep hardenability properties we have observed that this time increased to 16 and sometimes 17 minutes. We have felt that this was due to the fact that the bar was austenitic longer because of the lower transformation temperature and since the austenite is a poorer heat conductor than ferrite plus carbide a longer cooling time ensued. Since at the cooling rates involved nearly all the steels are austenitic at 1300 degrees Fahr., there would be very little effect on the cooling rate at 1300 degrees Fahr. Higher

carbon steels however do have slower cooling rates because they have a lower heat conductivity.

The author wishes to thank Mr. McQuaid for his complimentary remarks about our standard hardenability test. In this test we attempt to have a water temperature of 75 degrees Fahr. although we have found that no appreciable difference is obtained when the water temperature is kept between 70 and 80 degrees Fahr.

It is true that the type L bar, for steels of low hardenability, requires greater care in its fabrication than the standard bar. Nevertheless, no complicated machine operations are required and unless a machinist is very careless no trouble need be experienced. The bar may be any length between 2 and 4 inches without appreciably affecting the results.

Mr. McQuaid brings up a rather interesting point to account for differences in hardenability of steels of similar compositions. The paper by G. T. Williams submitted at this convention presents a good case for this point of view. Whatever may be the reason for the difference in hardenability behavior of steels of similar composition, the fact that these differences exist seems to be pretty well demonstrated.

The author appreciates the interest shown by those taking part in the discussion.

CHARACTERISTICS OF 5.0 AND 7.0 PER CENT CHROMIUM STEELS WITH VARYING MOLYBDENUM AND VANADIUM CONTENT

By W. G. Hildorf, C. L. Clark and A. E. White

Abstract

This paper presents results obtained from short-time tensile tests at room temperature and 1200 degrees Fahr., from rupture tests at 1200 degrees Fahr., and from a micro-examination of steels of the 5.0 and 7.0 per cent chromium types in which the molybdenum content varies from 0.50 to 2.0 per cent and the vanadium content from 0.0 to 1.0 per cent. Twenty-one steels are considered.

It is shown that in general the strength characteristics are continuously increased as the molybdenum content is varied over the given range while the strength characteristics are decreased when the vanadium content exceeds a given amount. An explanation for the difference in behavior of these two elements is advanced on the basis of their microstructures. Consideration is likewise given to the influence of the increase in the chromium content from 5.0 to 7.0 per cent.

IN the development of steels for high temperature applications it is generally recognized that certain of the carbide-forming elements, such as chromium, molybdenum and vanadium, are the most effective in improving the strength characteristics. No systematic investigation has, however, been undertaken to determine the influence of varying additions of these elements and this is particularly true with molybdenum and vanadium. In the case of chromium the influence of variations from 0.0 to 5.0 is fairly well established and extensive work now in progress in several laboratories on steels of the 5.0 to 9.0 per cent type will extend this range.

Insofar as molybdenum is concerned, the amount of this element in most high temperature steels has been confined to 0.50 per cent although some work has been done on plain carbon steels containing

A paper presented before the Twenty-first Annual Convention of the Society held in Chicago, October 23 to 27, 1939. Of the authors, W. G. Hildorf is chief metallurgical engineer, The Timken Roller Bearing Company, Canton, Ohio, and C. L. Clark and A. E. White are research engineer and director, respectively, Department of Engineering Research, University of Michigan, Ann Arbor. Manuscript received June 24, 1939.

1.0 and 1.5 per cent of this element and on certain alloy steels containing 1.0 per cent. Little information is available with respect to vanadium additions in excess of 0.30 per cent.

The present paper considers the influence of variations in the molybdenum content from 0.50 to 2.0 per cent, and in the vanadium content from 0 to 1.0 per cent, on certain of the physical characteristics of two types of alloy steels containing 5.0 and 7.0 per cent chromium. These two particular chromium contents were selected since the 5.0 per cent type has found extensive use for the past several years and considerable interest is now being shown in the higher chromium steels, especially for certain oil refinery applications.

Since molybdenum and vanadium, as well as chromium and silicon, are gamma loop formers, and thus cause the appearance of delta iron or free ferrite when their combined addition exceeds a certain amount, considerable attention was given to the microstructures of these steels and attempts made to correlate the physical properties with the structures.

Steels Investigated

The steels required for this investigation were made by the Timken Steel and Tube Division of The Timken Roller Bearing Company. All of the vanadium-bearing steels as well as the molybdenum steels containing 1.5 and 2.0 per cent of this element were made in an induction furnace, while the remaining ones were melted in commercial electric-arc furnaces. This difference in the method of manufacture may influence the magnitude of certain of the values obtained but it is not believed that it will change the trends developed. This belief is substantiated by values obtained from both induction and commercial heats of Si-Cr-Mo 7 and Si-Cr-Mo 7 + 1.0 Mo steels.

The chemical composition, heat treatment and Brinell hardness of the twenty-one steels considered are given in Table I. On the basis of chemical composition, these steels may be divided into five groups. In three of the groups the molybdenum content is varied through the steps of 0.5, 1.0, 1.5 and 2.0 per cent and the groups differ in that one contains 7.0 per cent chromium and the other two 5.0 per cent. These latter two groups differ in that one contains 0.50 to 1.0 per cent silicon and the other 1.0 to 1.5 per cent of this element. In the remaining two groups the vanadium

Table I

Chemical Composition, Heat Treatment and Brinell Hardness of 5.0 and 7.0 Per Cent Chromium Steels with Varying Molybdenum and Vanadium Content

Steel Designation	Chemical Composition, Per Cent C	Mn	Si	Cr	Mo	V	Heat-Treatment Degrees Fahr.	Brinell Hardness
Steels with Varying Molybdenum Content								
Si-Cr-Mo 7	0.11	0.43	0.92	7.33	0.59	....	N. 1750, D. 1500	174
Si-Cr-Mo 7 + 1.0 Mo	0.12	0.38	0.82	7.29	1.10	....	N. 1750, D. 1500	179
Si-Cr-Mo 7 + 1.5 Mo	0.12	0.32	0.88	7.47	1.51	....	N. 1750, D. 1500	183
Si-Cr-Mo 7 + 2.0 Mo	0.12	0.31	0.88	7.54	2.05	....	N. 1750, D. 1500	187
Si-Cr-Mo 5	0.11	0.40	0.93	5.24	0.59	....	Ann. 1550	167
Si-Cr-Mo 5 + 1.0 Mo	0.12	0.39	0.87	5.22	0.99	....	Ann. 1550	159
Si-Cr-Mo 5 + 1.5 Mo	0.12	0.31	0.95	5.34	1.48	....	N. 1750, D. 1500	174
Si-Cr-Mo 5 + 2.0 Mo	0.12	0.32	0.93	5.30	2.03	....	N. 1750, D. 1500	187
Si-Cr-Mo 5S	0.10	0.38	1.55	4.83	0.51	....	Ann. 1550	156
Si-Cr-Mo 5S + 1.0 Mo	0.10	0.37	1.37	5.16	0.89	....	Ann. 1550	173
Si-Cr-Mo 5S + 1.5 Mo	0.12	0.31	1.41	5.42	1.46	....	N. 1750, D. 1500	179
Si-Cr-Mo 5S + 2.0 Mo	0.11	0.32	1.41	5.41	2.00	....	N. 1750, D. 1500	197
Steels with Varying Vanadium Content								
Si-Cr-Mo 7M	0.12	0.38	0.82	7.29	1.10	....	N. 1750, D. 1500	179
Si-Cr-Mo 7M + 0.25 V	0.12	0.42	0.80	7.53	1.02	0.18	N. 1750, D. 1500	187
Si-Cr-Mo 7M + 0.50 V	0.12	0.39	1.01	7.62	1.08	0.56	N. 1750, D. 1500	170
Si-Cr-Mo 7M + 0.75 V	0.12	0.40	1.00	7.62	1.05	0.82	N. 1750, D. 1500	163
Si-Cr-Mo 7M + 1.00 V	0.10	0.36	0.90	7.70	1.09	1.06	N. 1750, D. 1500	169
Si-Cr-Mo 5M	0.12	0.39	0.87	5.22	0.99	....	Ann. 1550	159
Si-Cr-Mo 5M + 0.50 V	0.14	0.42	1.06	5.33	1.01	0.52	N. 1750, D. 1500	170
Si-Cr-Mo 5M + 0.75 V	0.14	0.39	1.03	5.30	1.08	0.69	N. 1750, D. 1500	170
Si-Cr-Mo 5M + 1.00 V	0.10	0.38	1.00	5.22	1.07	1.06	N. 1750, D. 1500	152

Note: The drawing time at 1500 degrees Fahr. was 6 hours in all cases.

content is varied from 0 to 1.0 per cent, with one group containing 5.0 per cent chromium and the other 7.0 per cent.

All of the vanadium-bearing steels, the 7.0 per cent chromium steels and the 5.0 per cent chromium steels containing 1.5 and 2.0 per cent molybdenum were normalized from 1750 degrees Fahr. and drawn at 1500 degrees Fahr. for 6 hours. The 5.0 per cent chromium steels containing up to 1.5 per cent molybdenum were annealed from 1550 degrees Fahr. (845 degrees Cent.). These heat treatments were purposely varied in order to conform to what would undoubtedly be commercial practice for producing the desired Brinell hardness. The hardness values of the heat treated steels ranged from 152 to 197 Brinell.

Results

The influence of variations in the molybdenum and vanadium contents on the physical characteristics of 5.0 and 7.0 per cent chromium steels is determined on the basis of tensile tests at room temperature and 1200 degrees Fahr., stress-rupture tests at 1200 degrees Fahr. and a metallographic examination of the steels in the given condition of heat treatment. The particular temperature

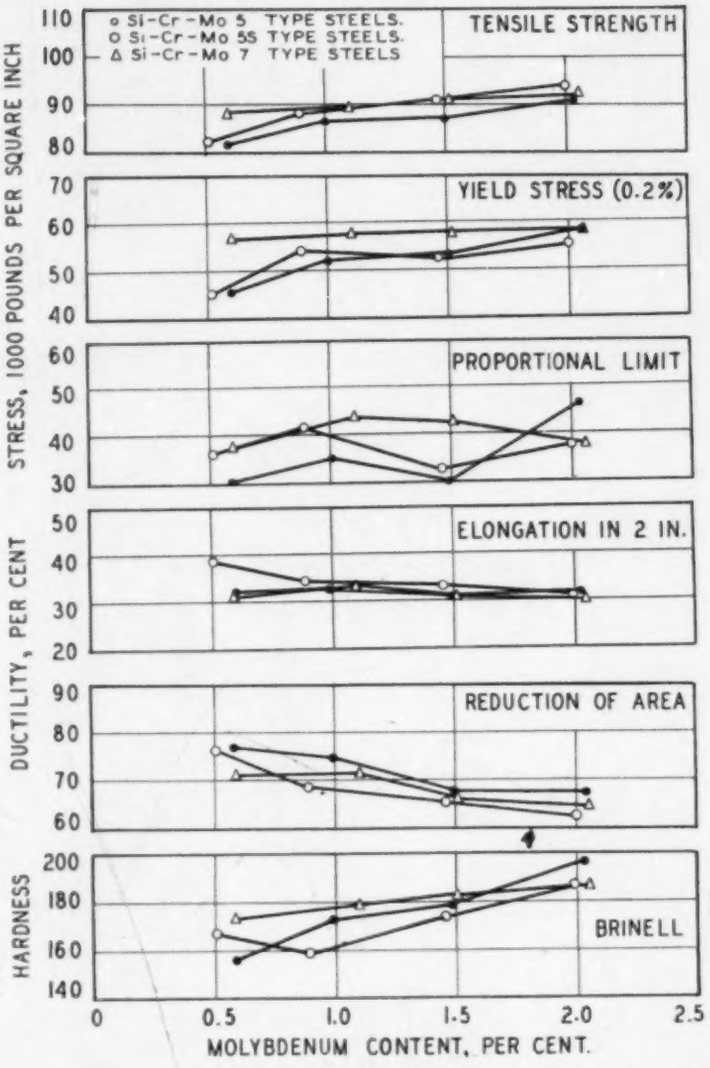


Fig. 1—Influence of Varying Molybdenum Content on the Room Temperature Physical Properties of 5.0 and 7.0 Per Cent Chromium Steels.

of 1200 degrees Fahr. was chosen for this investigation since it is one of considerable interest in certain refinery applications. Complete investigations are, however, in progress on certain of these steels over a wide temperature range but all of these findings are not as yet available.

Room Temperature Physical Properties—The room temperature physical properties of these steels are summarized in Figs. 1 and 2 with the results being so arranged as to show the influence of variations in the molybdenum and vanadium contents. Each of the reported values is the average of two tests.

First considering the influence of variations in the molybdenum

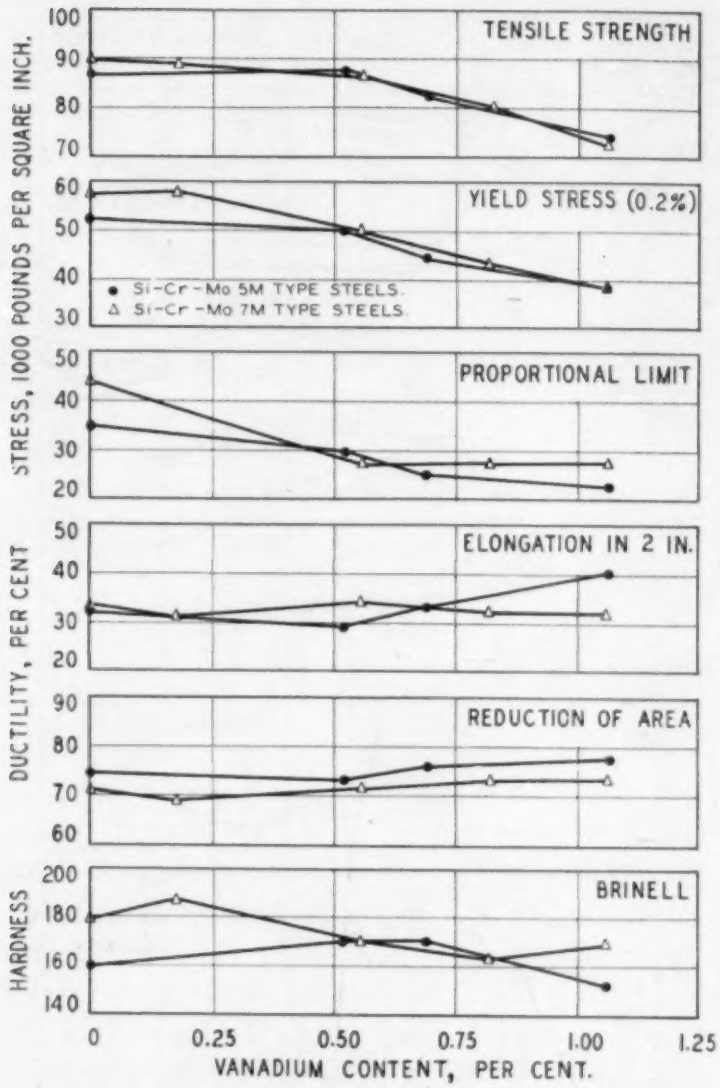


Fig. 2—Influence of Varying Vanadium Content on the Room Temperature Physical Properties of 5.0 and 7.0 Per Cent Chromium Steels.

content, Fig. 1, it is found that with these three types of steels the strength characteristics and hardness tend to increase, and the ductility to decrease, as the molybdenum content is raised from 0.50 to 2.0 per cent. The chief exception to this trend occurs in the proportional limit as this value reaches a maximum in all three steels at about 1.0 per cent molybdenum, followed by a second maximum at 2.0 per cent molybdenum with the two 5.0 per cent chromium steels.

In no case is the change in the physical characteristics of a very large order of magnitude, for with the tensile strength the maximum range is from 81,500 to 94,000 pounds per square inch, with

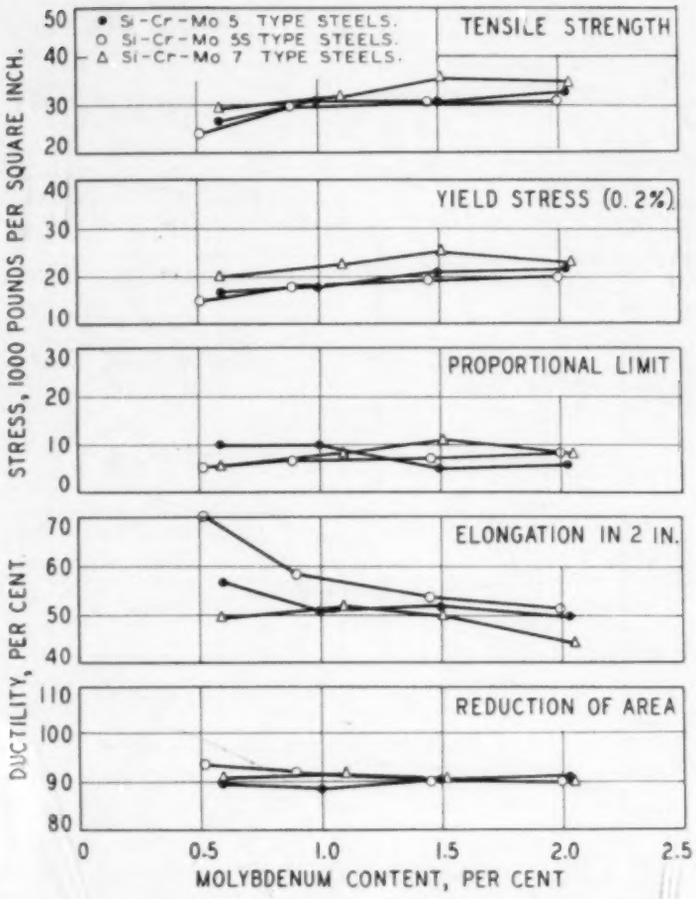


Fig. 3—Influence of Varying Molybdenum Content on the Tensile Properties at 1200 Degrees Fahr. of 5.0 and 7.0 Per Cent Chromium Steels.

the yield stress from 45,000 to 58,000 pounds per square inch, and with the elongation from 30 to 39 per cent. The variations observed are less pronounced in the 7.0 per cent chromium steel than in the two 5.0 per cent chromium steels, thus indicating the changes in composition to be less effective in the higher alloy steels.

Variations in the vanadium content, Fig. 2, do not exert the same influence on the room temperature physical characteristics as did variations in the molybdenum content, for with both types of steel the strength characteristics tend to decrease, and the ductility to increase, especially as the vanadium content exceeds 0.50 per cent. The degree of change is likewise more pronounced than in the case of the molybdenum variations for the tensile strength ranges from 72,000 to 89,500 pounds per square inch, the yield stress from 38,500 to 57,500 pounds per square inch, and the elongation from 29.5 to 40.5 per cent. Another point of difference lies in the fact that with

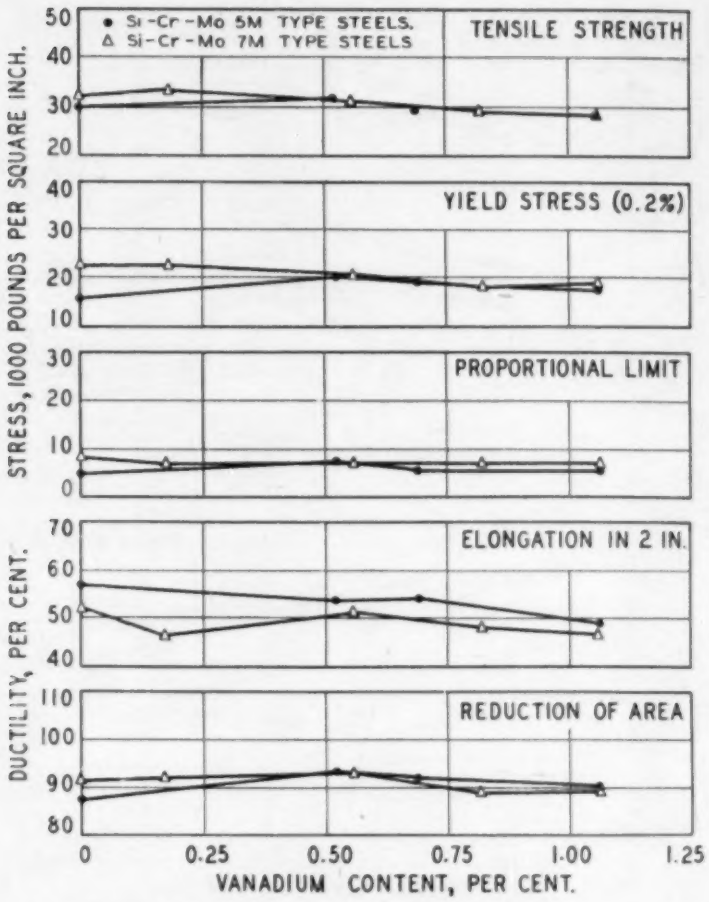


Fig. 4—Influence of Varying Vanadium Content on the Tensile Properties at 1200 Degrees Fahr. of 5.0 and 7.0 Per Cent Chromium Steels.

varying vanadium content the degree of change is of the same order of magnitude for both the 5.0 and 7.0 per cent chromium steels.

From these findings it follows that even though molybdenum and vanadium are both of the carbide forming type and are likewise both gamma loop formers, variations in their addition do not produce the same influence on the resulting room temperature physical properties. The microstructures of these steels, to be discussed later, afford an explanation for this observed difference.

Tensile Properties at 1200 Degrees Fahr.—As evidenced by the results of Figs. 3 and 4, the variations in the molybdenum and vanadium content exert the same general trends at 1200 degrees Fahr. as at room temperature, although the changes are of a lower order of magnitude. That is, increasing molybdenum content tends to increase the strength and lower the ductility, while increasing vanadium content tends to decrease the strength.

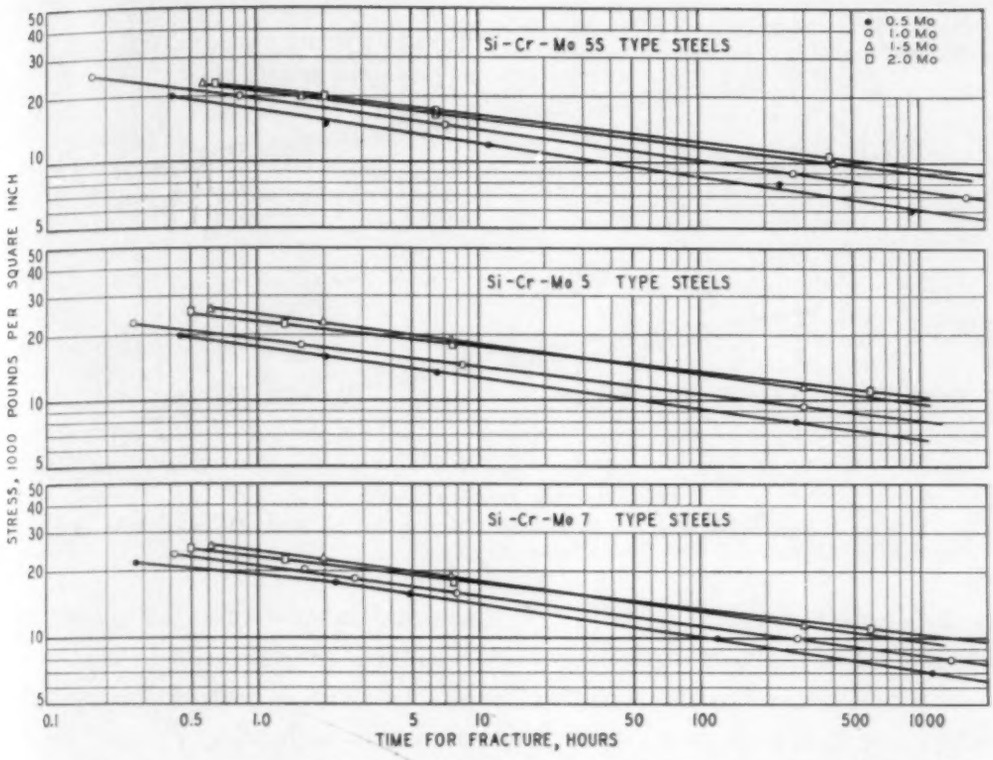


Fig. 5—Influence of Varying Molybdenum Content on the 1200 Degrees Fahr. Rupture Strength of 5.0 and 7.0 Per Cent Chromium Steels.

There are certain exceptions to these trends. With the vanadium steels the variation in composition had little if any influence on the proportional limit and reduction of area values. Likewise in the case of the 5.0 per cent chromium steel, the first addition of vanadium caused a slight increase in the tensile strength and yield stress values. With the molybdenum steels, a maximum occurred in the strength characteristics of the 7.0 per cent chromium steel at about 1.5 per cent molybdenum.

In the case of the molybdenum steels, chromium content likewise exerts an influence on the physical properties with the 7.0 per cent chromium steels tending to possess the higher strength values especially when the molybdenum content is 1.5 per cent or higher. With the vanadium steels, however, the 5.0 and 7.0 per cent chromium steels possessed almost identical values when the vanadium content was 0.50 per cent or higher.

Rupture Strength at 1200 Degrees Fahr.—Stress-rupture tests were conducted on each of these steels at 1200 degrees Fahr. In these tests, standard 0.505-inch diameter tensile specimens are subjected to fixed loads and the tests continued until actual fracture oc-

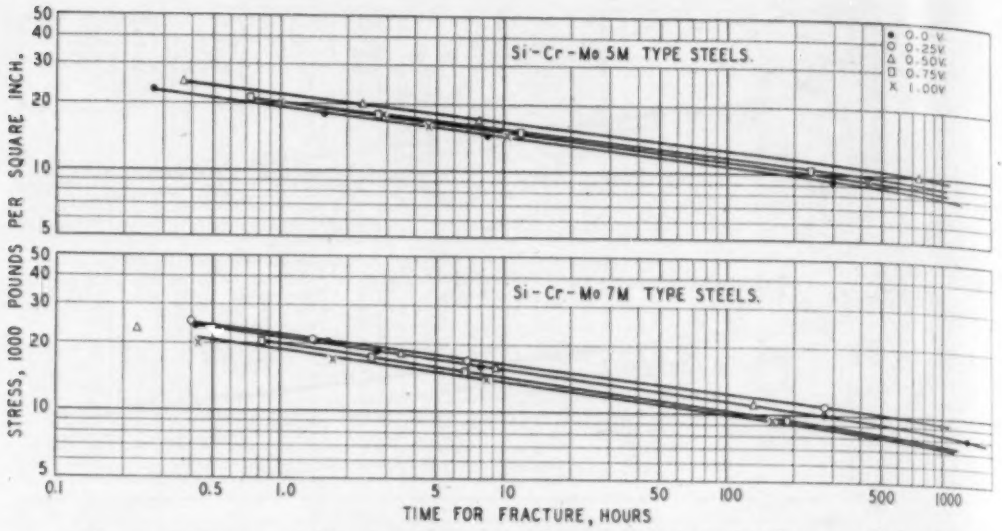


Fig. 6—Influence of Varying Vanadium Content on the 1200 Degrees Fahr. Rupture Strength of 5.0 and 7.0 Per Cent Chromium Steels.

curs. The stresses are so adjusted that the fracture time period varies from a few minutes up to several hundred hours.

Since the primary purpose of the present investigation was to determine the influence of variations in the molybdenum and vanadium content on steels of otherwise the same general type composition, certain of the tests were conducted for maximum time periods of only 200 to 500 hours. For each of the steel types, however, one series of tests was continued for longer time periods in order to establish the relationship more completely. Likewise tests have been conducted for time periods up to a minimum of 1000 hours on at least one steel of each type at 1300 degrees Fahr. in order to be sure that the straight-line logarithmic relationship at 1200 degrees Fahr., to be discussed later, would apply for fracture time periods in excess of 1000 hours.

Stress Versus Time—The results obtained from each of the individual fracture tests are summarized in Tables II and III and the stresses and corresponding fracture-time periods are plotted to logarithmic co-ordinates in Figs. 5 and 6. In both the tables and the figures the steels are subdivided into five groups.

The logarithmic method of plotting has been employed since, on the basis of previous work, it is known that this method of presentation results in a straight-line relationship between stress and fracture time provided the steel possesses a sufficient degree of surface and structural stability. Furthermore, it is known that such a straight-line relationship will exist with the 5.0 and 7.0 per cent

Table II

Stress-Rupture Characteristics at 1200 Degrees Fahr. of 5.0 and 7.0 Per Cent Chromium Steels with Varying Molybdenum Content

Molybdenum Content	Stress Lbs./Sq.In.	Time for Fracture Hour	Elongation in 2 In. Per Cent	Reduction of Area Per Cent
		Si-Cr-Mo 7 Type Steels		
0.59	29,250	S.T.T.S.	48.5	90.3
	22,000	0.28	46.5	89.4
	18,000	2.27	55.5	87.4
	16,000	4.88	45.0	87.4
	10,000	120.25	54.0	78.2
	7,000	1103.00	44.0	77.6
1.10	32,150	S.T.T.S.	50.0	91.8
	24,000	0.42	49.5	91.0
	20,500	1.65	53.5	90.1
	18,500	2.73	58.0	91.3
	16,000	7.96	58.0	91.0
	10,000	276.00	47.5	88.1
1.51	35,650	S.T.T.S.	50.0	90.5
	26,000	0.62	47.0	88.5
	23,000	1.98	46.0	88.3
	19,000	7.48	49.0	89.3
	11,500	297.0	43.0	86.3
2.05	34,500	S.T.T.S.	44.0	89.9
	25,500	0.50	44.0	89.1
	22,500	1.35	46.5	88.8
	18,000	7.65	49.0	89.3
	11,000	598.0	45.5	86.3
		Si-Cr-Mo 5 Type Steels		
0.59	26,500	S.T.T.S.	57.0	89.7
	20,000	0.45	47.5	87.2
	16,000	2.05	56.0	83.3
	13,500	6.47	66.0	80.7
	8,000	276.00	59.5	76.8
0.99	30,750	S.T.T.S.	51.0	88.7
	23,000	0.27	55.0	88.4
	18,000	1.58	60.0	83.9
	14,500	8.48	61.0	84.2
	9,500	299.00	52.5	84.0
1.48	35,650	S.T.T.S.	50.0	90.5
	26,000	0.62	47.0	88.5
	23,000	1.98	46.0	88.3
	19,000	7.48	49.0	89.3
	11,500	297.00	43.0	86.3
2.03	34,500	S.T.T.S.	44.0	89.9
	25,500	0.50	44.0	89.1
	22,500	1.35	46.5	88.8
	18,000	7.65	49.0	89.3
	11,000	598.00	45.5	86.3
		Si-Cr-Mo 5S Type Steels		
0.51	24,000	S.T.T.S.	70.8	93.7
	20,000	0.41	63.0	93.1
	15,000	2.07	75.0	91.9
	12,000	11.15	74.5	88.4
	8,000	235.0	67.0	87.4
	6,000	927.0	75.0	91.0
0.89	29,900	S.T.T.S.	58.8	92.0
	25,000	0.17	56.0	90.2
	20,000	0.83	59.5	90.4
	15,000	7.17	65.5	88.0
	9,000	270.00	54.0	86.4
	7,000	1645.50	46.0	84.9
1.46	30,500	S.T.T.S.	54.0	90.3
	23,000	0.57	54.5	89.4
	20,000	1.60	57.0	90.1
	16,500	6.48	59.0	89.3
	10,000	410.00	46.0	86.1
2.00	30,750	S.T.T.S.	51.5	90.0
	23,000	0.65	52.0	88.4
	20,000	2.05	52.5	88.1
	17,000	6.42	51.0	87.6
	10,500	397.00	47.0	84.3

S.T.T.S. = Short-time tensile strength at 1200 degrees Fahr.

Table III

Stress-Rupture Characteristics of 5.0 and 7.0 Per Cent Chromium Steels with Varying Vanadium Content

Vanadium Content	Stress Lbs./Sq.In.	Time for Fracture Hour	Elongation in 2 In. Per Cent	Reduction of Area Per Cent
		Si-Cr-Mo 7M Type Steels		
0.0	32,150	S.T.T.S.	50.0	91.8
	24,000	0.42	49.5	91.0
	20,500	1.65	53.5	90.1
	18,500	2.73	58.0	91.3
	16,000	7.96	58.0	91.0
	10,000	276.00	47.5	88.1
0.18	33,250	S.T.T.S.	46.5	92.1
	25,000	0.40	45.0	89.4
	21,000	1.40	48.5	90.3
	17,000	6.90	46.0	91.2
	11,000	278.00	48.5	90.3
0.56	31,000	S.T.T.S.	51.5	93.0
	23,000	0.23	55.0	90.4
	18,000	3.50	58.0	92.3
	16,000	9.38	58.5	92.4
	11,000	131.50	50.0	91.9
0.82	29,250	S.T.T.S.	48.5	89.6
	20,500	0.83	52.5	88.7
	17,500	2.58	67.0	91.3
	15,000	6.79	53.5	91.3
	9,500	188.00	59.5	91.6
1.06	28,400	S.T.T.S.	47.0	89.9
	20,000	0.43	48.5	89.7
	17,000	1.71	59.0	87.5
	14,000	8.42	61.5	91.3
	9,500	163.50	51.0	92.0
		Si-Cr-Mo 5M Type Steels		
0.0	30,750	S.T.T.S.	51.0	88.7
	23,000	0.27	55.0	88.4
	18,000	1.58	60.0	83.9
	14,500	8.48	61.0	84.2
	9,500	299.00	52.5	84.0
0.52	31,750	S.T.T.S.	54.0	93.5
	25,000	0.37	53.5	92.1
	20,000	2.33	54.0	91.9
	17,000	7.55	68.0	92.4
	10,000	753.00	48.0	90.0
0.69	29,500	S.T.T.S.	54.5	92.1
	21,000	0.73	58.5	92.3
	18,000	2.71	55.5	91.6
	15,000	11.92	55.0	92.5
	10,500	240.00	57.0	91.6
1.06	28,000	S.T.T.S.	49.5	90.2
	20,000	1.00	48.0	88.7
	18,000	2.81	57.0	89.7
	16,000	4.60	48.0	91.3
	14,500	10.17	57.0	90.4
	7,500	426.50	69.0	90.3

S.T.T.S. = Short-time tensile strength at 1200 degrees Fahr.

chromium steels at 1200 degrees Fahr. provided their oxidation resistance is improved by the addition of a suitable amount of silicon. It was for this reason that all of the steels considered contained a minimum of 0.80 per cent silicon.

First considering the effect of varying molybdenum content, Fig. 5, it is found that a straight-line relationship exists for each of the three types of steels and that the rupture strength increases

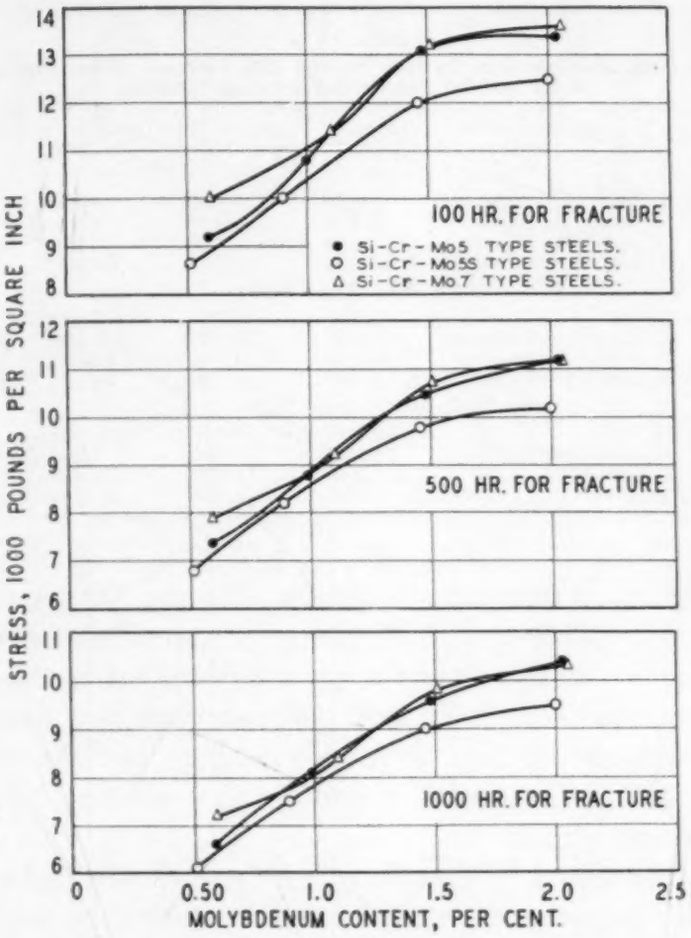


Fig. 7—Influence of Varying Molybdenum Content on 1200 Degrees Fahr. Rupture Strength of 5.0 and 7.0 Per Cent Chromium Steels.

with increasing molybdenum content. In the case of the Si-Cr-Mo 5S steels increasing molybdenum content raises the rupture strength over the complete range of fracture time periods. The same likewise is true with the remaining two types as the molybdenum content is increased to 1.5 per cent. However, a further increase in the molybdenum content to 2.0 per cent slightly decreases the strength for the shorter fracture time periods, but again increases it for the more prolonged time periods.

Varying vanadium content, Fig. 6, does not exert the same influence on the rupture strength as varying molybdenum content. With the 5.0 per cent chromium steels the rupture strength is increased by the addition of 0.50 per cent vanadium but is then decreased upon further additions of this element. In fact the steel containing 1.0 per cent vanadium is only slightly superior to the

Table IV

Influence of Varying Molybdenum Content on the 1200 Degrees Fahr. Rupture Strength of 5.0 and 7.0 Per Cent Chromium Steels

Molybdenum Content	Time for Fracture, Hours					
	1.0	10	100	250	500	1000
	Si-Cr-Mo 5S Type Steels					
0.51	17,500	12,200	8,650	7,600	6,800	6,150
0.89	19,500	14,100	10,250	9,100	8,200	7,500
1.46	20,200	15,900	12,000	10,750	9,800	9,000
2.00	20,800	16,400	12,500	11,200	10,200	9,500
	Si-Cr-Mo 5 Type Steels					
0.59	17,800	12,800	9,200	8,000	7,350	6,600
0.99	19,100	14,200	10,800	9,600	8,800	8,100
1.48	24,900	18,100	13,100	11,700	10,500	9,600
2.03	23,000	17,500	13,400	12,100	11,200	10,400
	Si-Cr-Mo 7 Type Steels					
0.59	19,200	14,200	10,000	8,800	7,900	7,200
1.10	21,200	15,500	11,400	10,000	9,200	8,400
1.51	25,000	18,100	13,200	11,800	10,750	9,800
2.05	23,200	17,900	13,600	12,200	11,200	10,300

steel containing no vanadium. Likewise with the 7.0 per cent chromium steel, the addition of 0.25 per cent vanadium improves the rupture strength slightly while further additions lower the strength. As a result the steel containing 0.50 per cent vanadium has the same rupture strength as the steel with no vanadium and the steels containing 0.75 and 1.0 per cent vanadium are inferior to the steel containing no vanadium.

The relationship of Figs. 5 and 6 permits the determination of the stresses corresponding to definite fracture-time periods, and values taken from these figures for fracture-time periods varying from 1.0 to 1000 hours are given in Tables IV and V. Figs. 7 and 8 show graphically the behavior of these steels for fracture-time periods of 100, 500 and 1000 hours.

For each of the three fracture-time periods considered increas-

Table V

Influence of Varying Vanadium Content on the 1200 Degrees Fahr. Rupture Strength of 5.0 and 7.0 Per Cent Chromium Steels

Vanadium Content	Time for Fracture, Hours					
	1.0	10	100	250	500	1000
	Si-Cr-Mo 5M Type Steels					
0.0	19,100	14,200	10,800	9,600	8,800	8,100
0.52	22,000	16,800	12,800	11,300	10,500	9,800
0.69	20,000	15,100	11,800	10,500	9,700	9,000
1.06	20,000	15,000	11,250	10,000	9,200	8,500
	Si-Cr-Mo 7M Type Steels					
0.0	21,200	15,500	11,400	10,000	9,200	8,400
0.18	21,800	16,250	12,400	11,000	10,100	9,400
0.56	21,200	15,500	11,400	10,000	9,200	8,400
0.82	19,900	14,300	10,400	9,200	8,300	7,600
1.06	18,900	13,800	10,000	8,800	8,000	7,350

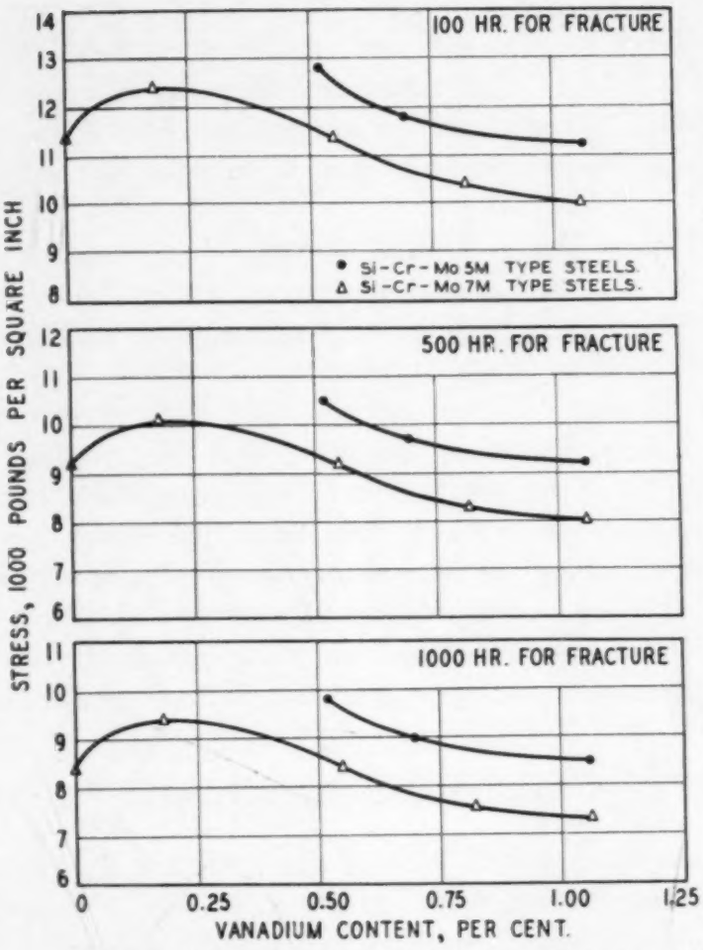


Fig. 8—Influence of Varying Vanadium Content on the 1200 Degrees Fahr. Rupture Strength of 5.0 and 7.0 Per Cent Chromium Steels.

ing molybdenum content, Fig. 7, increases the rupture strength with the degree of increase being the more pronounced as the molybdenum content is raised from 0.50 to 1.50 per cent. Likewise with molybdenum additions of 1.0 and higher, the strength of the Si-Cr-Mo 5 and Si-Cr-Mo 7 steels is nearly identical, thus indicating that an increase in the chromium content from 5.0 to 7.0 per cent is not beneficial insofar as the rupture strength at 1200 degrees Fahr. under oxidizing conditions is concerned. The strength of the higher silicon 5.0 per cent chromium steel is inferior but such might not be the case under more severely oxidizing conditions or for more extended fracture-time periods.

With varying vanadium content, Fig. 8, the rupture strength for each of the three time periods considered is increased with the first addition of vanadium and is then decreased as the amount of

this element is further increased. With the 7.0 per cent chromium steels this decrease occurs as the vanadium exceeds 0.18 per cent, and with the 5.0 per cent chromium steels, as it exceeds 0.50 per cent. For each of the vanadium contents considered, except 0.0 per cent, the 5.0 per cent chromium steel is superior to the 7.0 per cent type.

Time Versus Ductility—The ductility characteristics of each of the stress-rupture specimens is likewise given in Tables II and III in order to show the combined influence of time and stress on the hot ductility of these steels at 1200 degrees Fahr.

All of the steels considered possessed high elongation and reduction of area values, thus indicating that they would be capable of a high degree of deformation at 1200 degrees Fahr. before actual fracture occurred. In fact in most cases the elongation value of the specimen requiring the maximum time for fracture was in good agreement with the corresponding value from the short-time tensile test. The minimum elongation value obtained with the molybdenum steels was 43.0 per cent and with the vanadium steels 48.0 per cent.

Metallographic Examination

The microstructures of each of the steels are shown, at a magnification of 100 diameters, in Figs. 9 to 13, inclusive. The structures shown apply only for the given condition of heat treatment and it is entirely possible that certain of them at least might be capable of revision under other types of treatment. The heat treatment used, however, would be considered as commercial for these types of steels. In each figure the photomicrographs are arranged so as to show the influence of variations in either the molybdenum or vanadium contents.

Figs. 9, 10 and 11 show the influence of variations in the molybdenum content from 0.50 to 2.0 per cent on the microstructures of the two 5.0 per cent chromium and the 7.0 per cent chromium steels. With the lower silicon 5.0 per cent chromium steel and the 7.0 per cent chromium steel, delta iron, or untransformed ferrite, does not make its appearance until 2.0 per cent molybdenum is present. Even with this amount of molybdenum the amount of delta iron present is very small, although as should be expected it is present to a greater extent in the 7.0 per cent than in the 5.0 per cent chromium steel. With the higher silicon 5.0 per cent

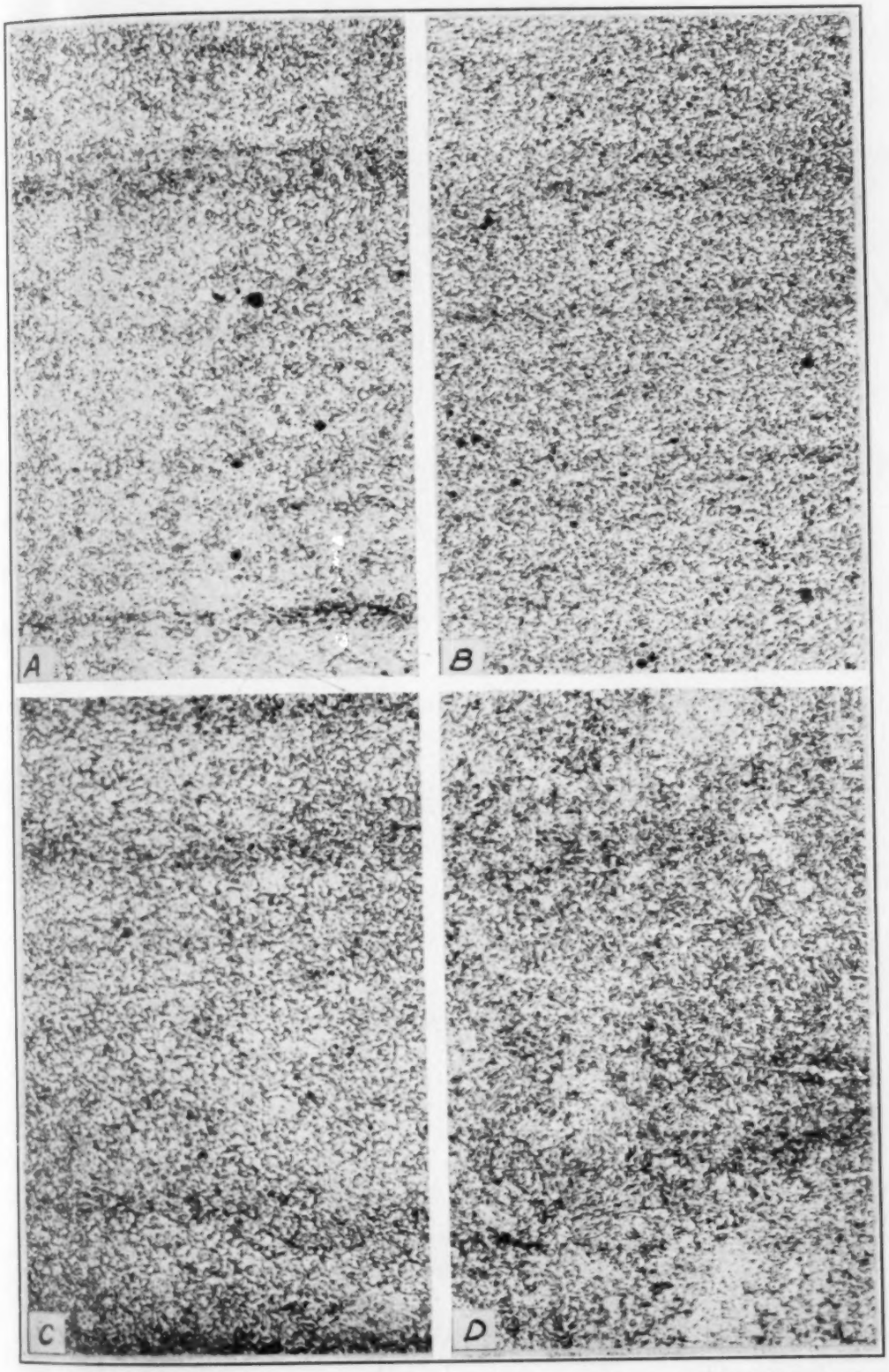


Fig. 9—Microstructures of Si-Cr-Mo 5 Type Steels with Varying Molybdenum Content. × 100.
Fig. 9a—0.59 Per Cent Molybdenum. Fig. 9b—0.99 Per Cent Molybdenum.
Fig. 9c—1.48 Per Cent Molybdenum. Fig. 9d—2.03 Per Cent Molybdenum.

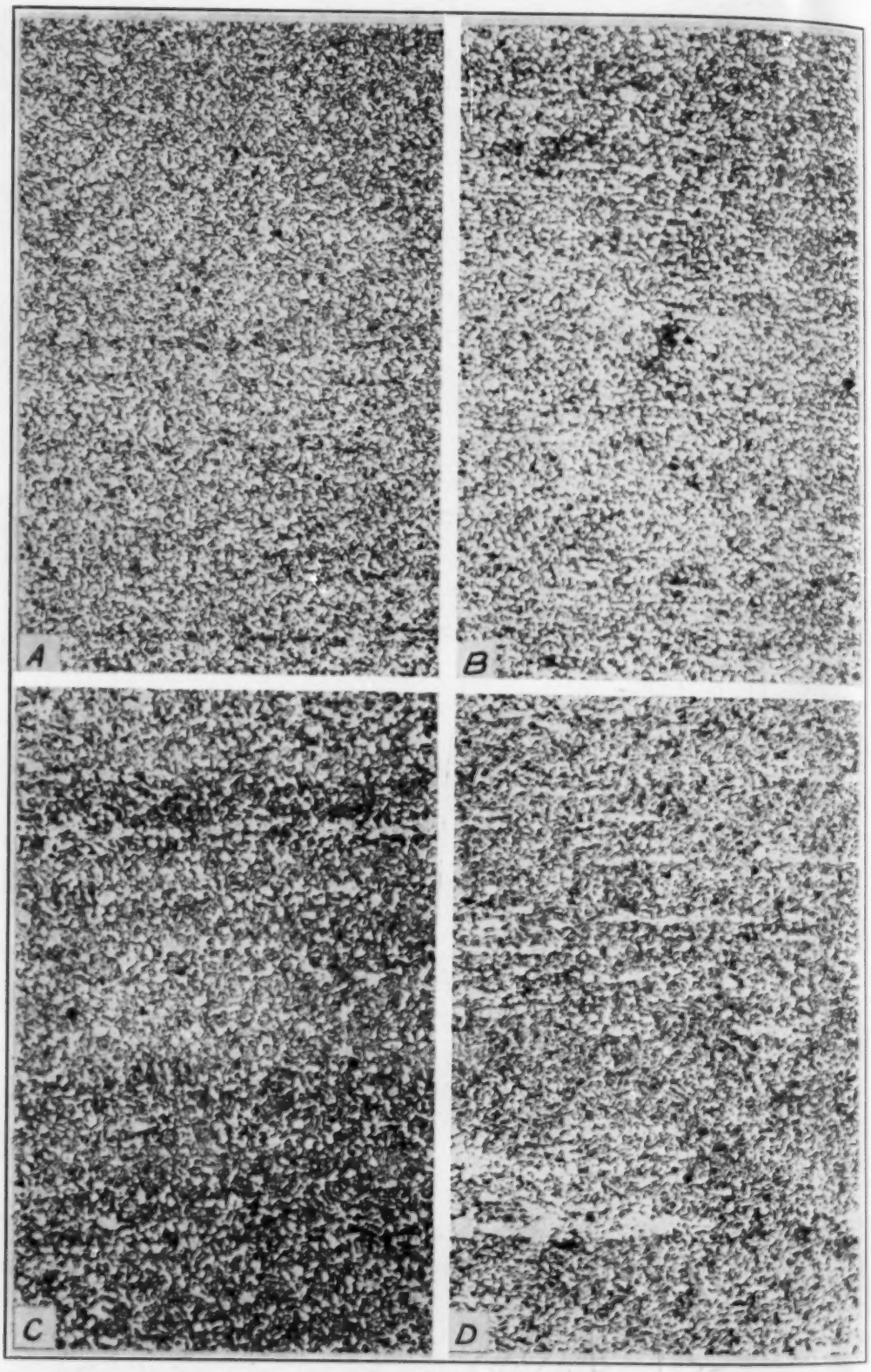


Fig. 10—Microstructures of Si-Cr-Mo 5S Type Steels with Varying Molybdenum Content. × 100.
Fig. 10a—0.51 Per Cent Molybdenum. Fig. 10b—0.89 Per Cent Molybdenum.
Fig. 10c—1.46 Per Cent Molybdenum. Fig. 10d—2.00 Per Cent Molybdenum.

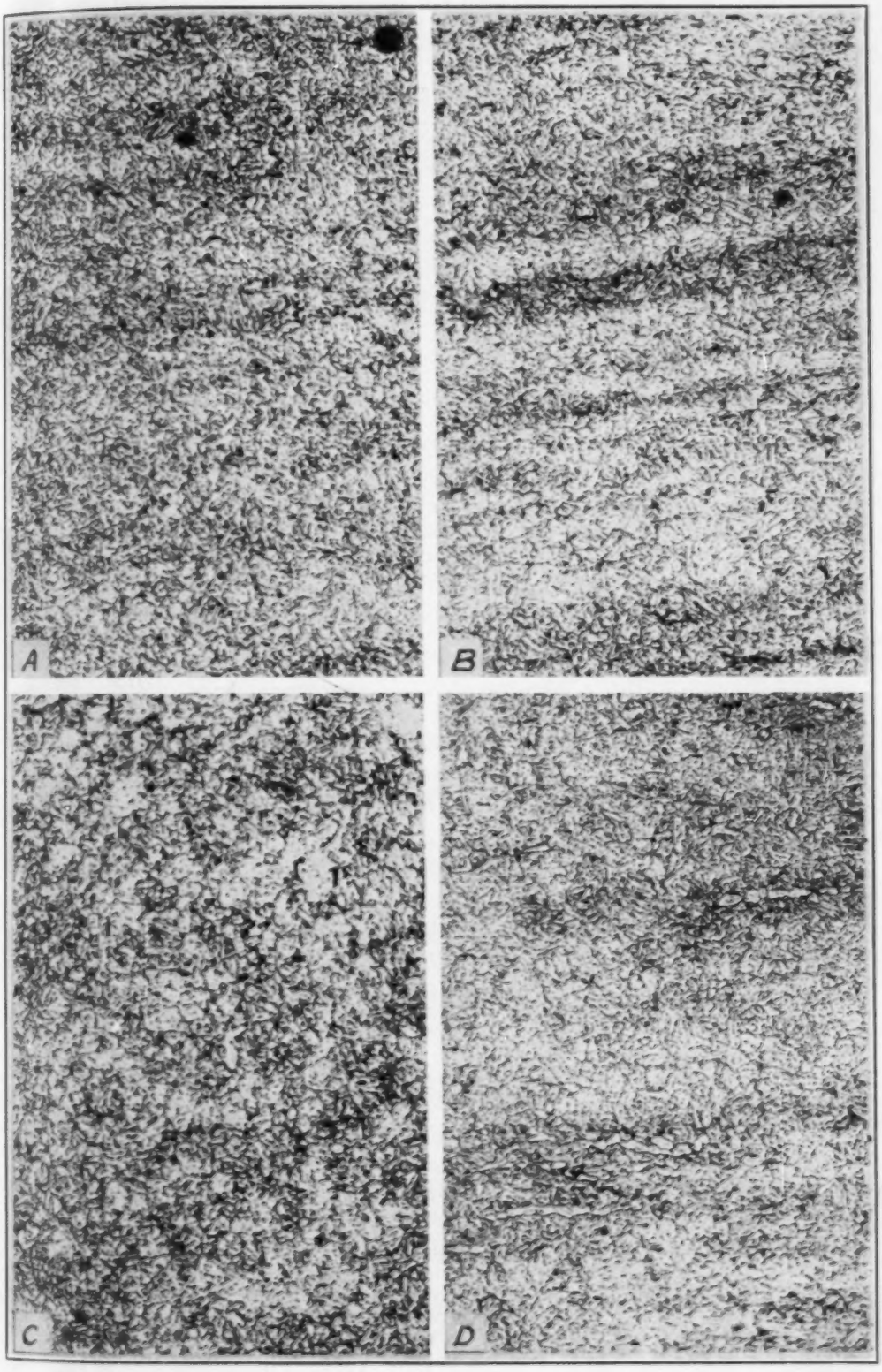


Fig. 11—Microstructures of Si-Cr-Mo 7 Type Steels with Varying Molybdenum Content. × 100.
Fig. 11a—0.59 Per Cent Molybdenum. Fig. 11b—1.10 Per Cent Molybdenum.
Fig. 11c—1.51 Per Cent Molybdenum. Fig. 11d—2.05 Per Cent Molybdenum.

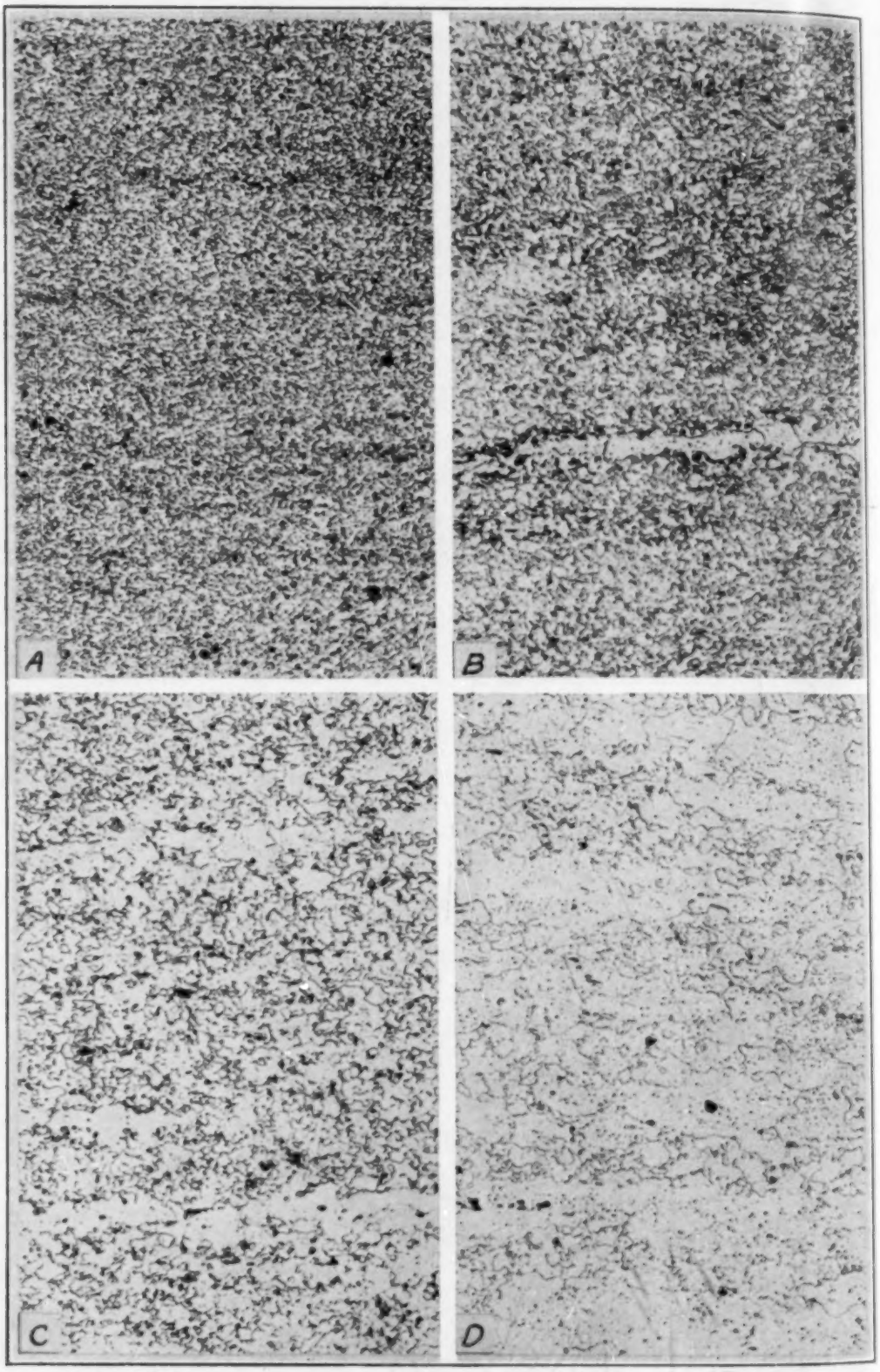
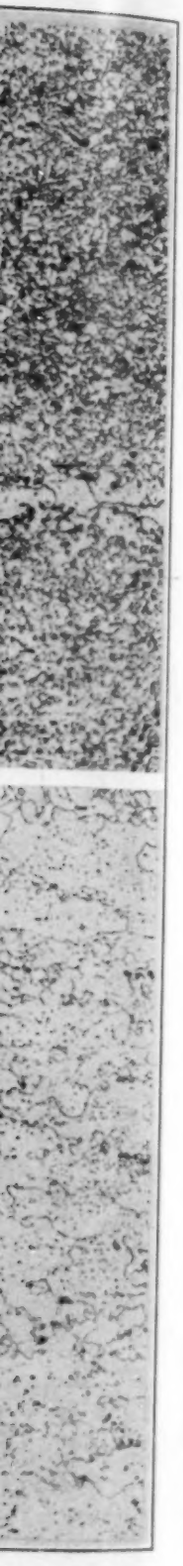


Fig. 12—Microstructures of Si-Cr-Mo 5 Type Steels with Varying Vanadium Content. × 100.
Fig. 12a—0.99 Per Cent Molybdenum.
Fig. 12b—1.01 Per Cent Molybdenum, 0.52 Per Cent Vanadium.
Fig. 12c—1.08 Per Cent Molybdenum, 0.69 Per Cent Vanadium
Fig. 12d—1.07 Per Cent Molybdenum, 1.06 Per Cent Vanadium



Vanadium Con-

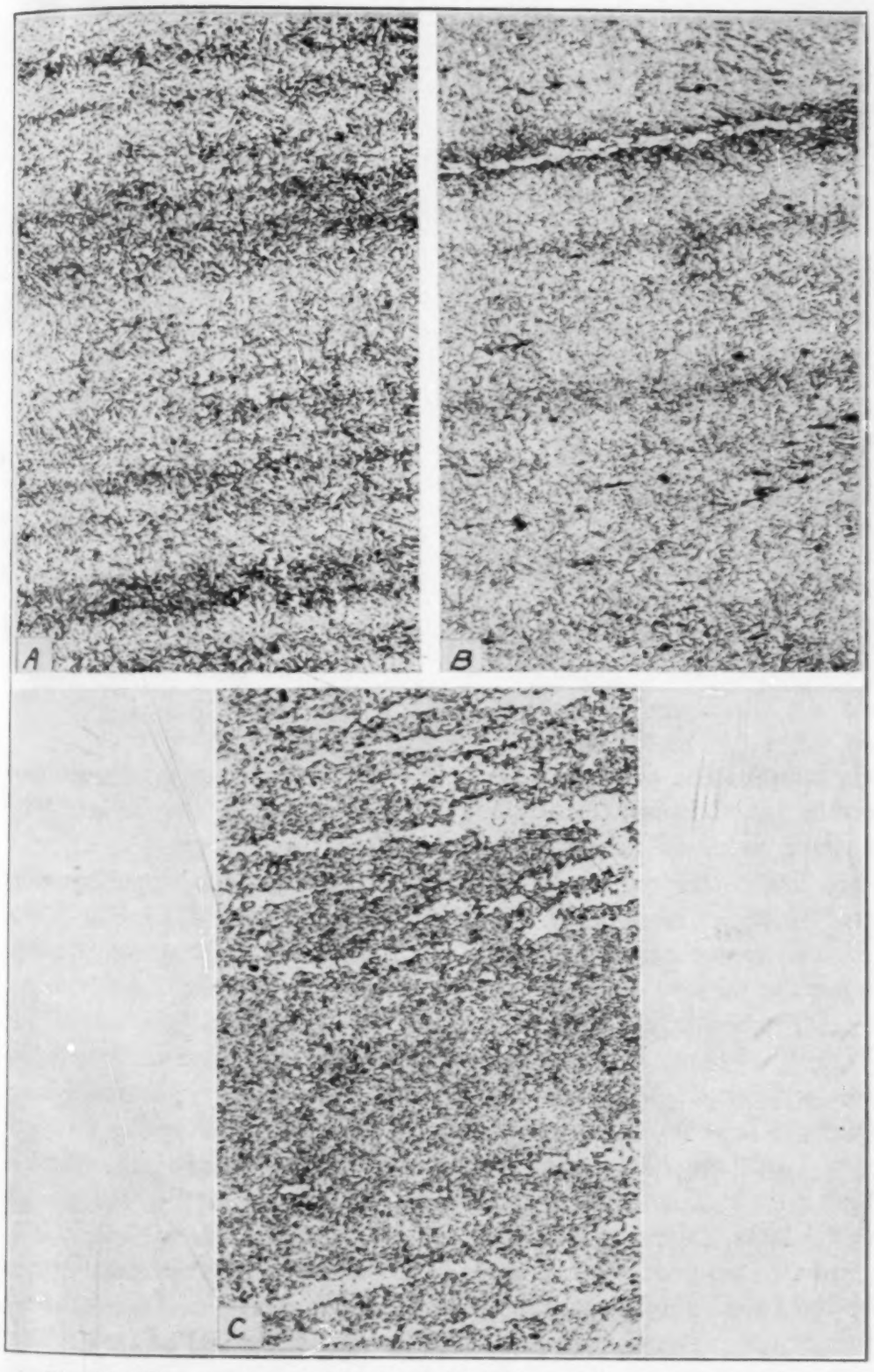


Fig. 13—Microstructures of Si-Cr-Mo 7 Type Steels with Varying Vanadium Content. × 100.
Fig. 13a—1.10 Per Cent Molybdenum.
Fig. 13b—1.02 Per Cent Molybdenum, 0.18 Per Cent Vanadium.
Fig. 13c—1.08 Per Cent Molybdenum, 0.56 Per Cent Vanadium.

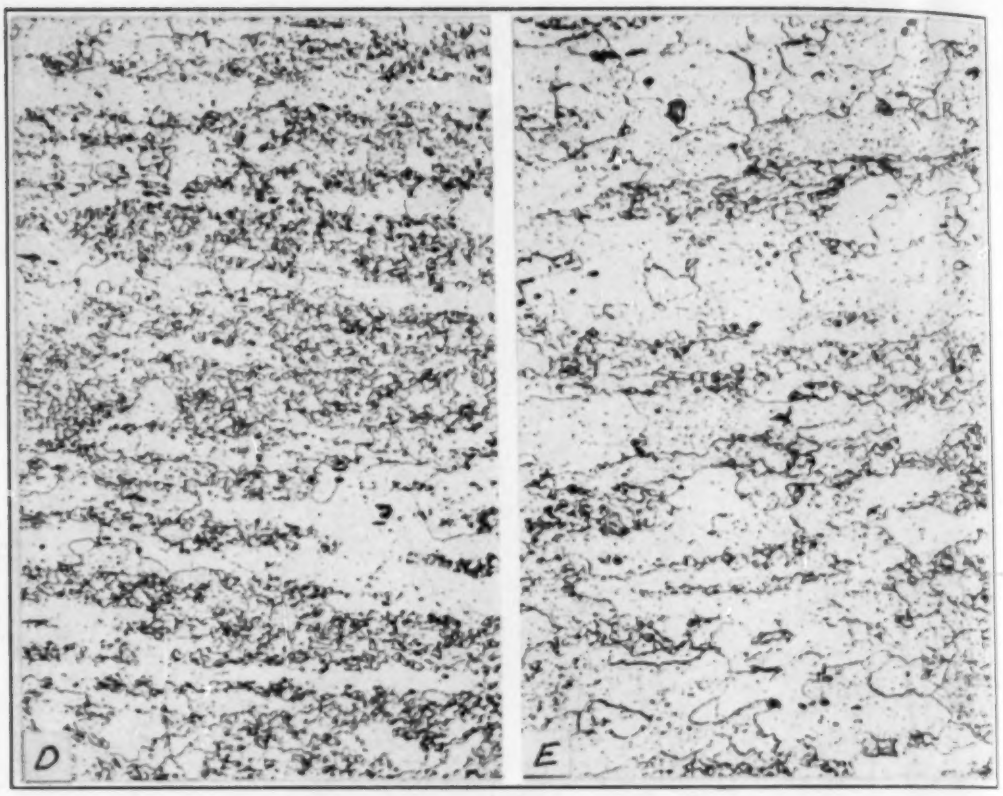


Fig. 13d—1.05 Per Cent Molybdenum, 0.82 Per Cent Vanadium.
Fig. 13e—1.09 Per Cent Molybdenum, 1.06 Per Cent Vanadium.

chromium steel, delta iron appears at 1.5 per cent molybdenum and as the molybdenum is further increased to 2.0 per cent a relatively large amount of this constituent is present.

The corresponding influence of variation in the vanadium content on the microstructures is shown in Figs. 12 and 13. With the 5.0 per cent chromium steel, a small amount of delta iron appears upon the addition of 0.50 per cent vanadium and the steel becomes almost completely ferritic when 1.0 per cent vanadium is present. With the 7.0 per cent chromium steel, delta iron first appears upon the addition of 0.18 per cent vanadium and the steel containing 0.80 per cent is almost completely ferritic.

These results clearly show the additive effect of the gamma loop forming elements in producing delta iron. In the absence of molybdenum, vanadium and silicon with a low carbon content it is generally assumed that about 12 to 14 per cent chromium is required to produce a ferritic steel. The structures of Fig. 10 show that in the presence of 1.5 per cent molybdenum and approximately 1.5 per cent silicon, delta iron appears with 5.0 per cent chromium even in the presence of 0.12 per cent carbon.

Table VI

Equivalent Chromium Content of 5.0 and 7.0 Per Cent Chromium Steels with Varying Molybdenum and Vanadium Content Based on Gamma Loop Tendencies

Steel Designation	Equivalent Chromium Content
Si-Cr-Mo 7	15.21
Si-Cr-Mo 7 + 1.00 Mo	16.61
Si-Cr-Mo 7 + 1.50 Mo	18.79
Si-Cr-Mo 7 + 2.00 Mo	21.02
Si-Cr-Mo 5	13.18
Si-Cr-Mo 5 + 1.00 Mo	15.40
Si-Cr-Mo 5 + 1.50 Mo	16.96
Si-Cr-Mo 5 + 2.00 Mo	19.00
Si-Cr-Mo 5S	16.17
Si-Cr-Mo 5S + 1.00 Mo	16.94
Si-Cr-Mo 5S + 1.50 Mo	19.72
Si-Cr-Mo 5S + 2.00 Mo	21.87
Steels with Varying Vanadium Content	
Si-Cr-Mo 7M	16.61
Si-Cr-Mo 7M + 0.25 V	18.57
Si-Cr-Mo 7M + 0.50 V	24.72
Si-Cr-Mo 7M + 0.75 V	27.66
Si-Cr-Mo 7M + 1.00 V	30.18
Si-Cr-Mo 5M	15.40
Si-Cr-Mo 5M + 0.50 V	21.97
Si-Cr-Mo 5M + 0.75 V	24.08
Si-Cr-Mo 5M + 1.00 V	28.22

Vanadium by itself is more powerful than molybdenum in its gamma loop forming tendencies and this likewise is true in the presence of chromium, silicon and carbon as evidenced by the fact that in the 7.0 per cent chromium steel, also containing 1.0 per cent molybdenum, only 0.18 per cent vanadium was required to cause the appearance of delta iron.

It is generally assumed that in carbonless iron the following percentages of these elements are required to close the gamma loop: chromium, 12.8 per cent; silicon, 2.2 per cent; molybdenum, 3.0 per cent; and vanadium, 1.0 per cent. This in turn implies that if the effect of these elements is entirely additive then silicon is approximately six times as effective as chromium in this respect, molybdenum four times as effective, and vanadium 12 times as effective.

Table VI gives the equivalent chromium content of these steels, assuming that the effect of molybdenum, vanadium and silicon is additive in their ability to close the gamma loop. In these calculations consideration was not given to either the carbon or manganese content since both of these elements are present in approximately constant amounts in each of the steels.

From Table VI it appears that insofar as the molybdenum steels are concerned, free ferrite, or delta iron, first makes its appearance with an equivalent chromium content of approximately 19. Likewise with the vanadium-bearing steels this value appears to be of

the same order of magnitude for with the 5.0 per cent chromium steels an appreciable amount of delta iron is present with an equivalent chromium content of about 22, and the same is true of the 7.0 per cent chromium steels with an equivalent chromium content of about 19.

It should be realized that the above relationship applies only to steels containing approximately 0.12 per cent carbon and 0.40 per cent manganese. The equivalent chromium content required to cause the appearance of delta iron would be decreased as the carbon content is lowered and somewhat increased as the manganese content is decreased. The appearance of delta iron may also be influenced by the hot fabrication process employed and by the rate of cooling from this temperature.

Discussion of Results

It was found that in general the strength characteristics of the 5.0 and 7.0 per cent chromium steels were increased at both room temperature and 1200 degrees Fahr. as the molybdenum content was increased from 0.5 per cent up to 2.0 per cent, while under the same conditions, the strength characteristics were decreased as the vanadium content exceeded a certain amount. A comparison of these results with the microstructures of the steels will indicate a possible cause as to the difference in the behavior of molybdenum and vanadium additions.

As the molybdenum content of the Si-Cr-Mo 5 and Si-Cr-Mo 7 steels was varied, delta iron did not appear until 2.0 per cent molybdenum was present and even then the amount of this constituent formed was relatively slight. Likewise the rupture strength of these steels increased continuously although the degree of increase was more pronounced up to 1.5 per cent molybdenum than it was as the molybdenum was further raised to 2.0 per cent. The same general conditions exist for the Si-Cr-Mo 5S steels except that delta iron appears with 1.5 per cent molybdenum.

With variations in the vanadium content, delta iron appears in the 5.0 per cent chromium steels at 0.52 per cent vanadium and in the 7.0 per cent chromium steels with 0.18 per cent vanadium. With further additions the amount of delta iron present increases rapidly. Likewise the rupture strength at 1200 degrees Fahr. decreases as the vanadium content exceeds that necessary to cause the appearance of the first delta iron.

It would appear therefore that the presence of delta iron in relatively large amounts causes a decrease in the strength characteristics. This is especially pronounced in the case of the rupture strength at 1200 degrees Fahr. but also applies to the short-time strength characteristics at both room temperatures and 1200 degrees Fahr.

Conclusions

The results obtained permit the following conclusions with respect to the influence of variations in the molybdenum and vanadium content on certain of the characteristics of 5.0 and 7.0 per cent chromium steels:

1. The short-time strength characteristics at room temperature and 1200 degrees Fahr., and the rupture strength at 1200 degrees Fahr. are in general continuously increased as the molybdenum content is varied through steps of about 0.50, 1.0, 1.5 and 2.0 per cent.

2. These same characteristics are in general increased upon the first addition of vanadium but are then decreased as the vanadium exceeds a certain amount. In the case of the 5.0 per cent chromium steels, the trend changes at 0.50 per cent vanadium, and with the 7.0 per cent chromium steels at 0.18 per cent vanadium.

3. The microstructures show that in the lower silicon steels, delta iron does not appear until 2.0 per cent molybdenum is present while only 0.18 per cent vanadium is sufficient to cause the appearance of this constituent in the 7.0 per cent chromium steels, and 0.5 per cent in the 5.0 per cent chromium steels.

4. A relationship is believed to exist between the strength characteristics and the microstructures in that the strength decreases as the amount of delta iron exceeds a certain amount. It is for this reason that vanadium additions in excess of a given amount decrease, rather than increase, the strength.

5. Variations in the chromium content did not exert the same influence on the 1200 degrees Fahr. rupture strength of the molybdenum and vanadium-bearing steels. For the same silicon content an increase in the chromium content from 5.0 to 7.0 per cent did not appreciably influence the rupture strength of the steels containing 1.0 per cent or more molybdenum while it decreased the rupture strength of all the steels containing vanadium.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to The Timken Roller Bearing Company for the financial assistance which made this investigation possible and for the permission to publish the findings.

DISCUSSION

Written Discussion: By Turner C. Smith, engineer, General Petroleum Corp., Los Angeles.

To a user of chromium-molybdenum steels in oil refinery service, this paper is of very timely interest. The data and photomicrographs answer the frequent question, "If a small amount of a certain element is good, would not more be better?".

While my metallurgical knowledge and experiences are insufficient for searching comments on this excellent paper, I do wish to ask certain questions, typical of the layman, for the authors' consideration:

(1) Are these alloys stable without further banding of the delta iron when heated for long periods of time at high temperatures? Specific time-temperatures in mind are 25,000 hours at 1200 degrees Fahr., 5000 hours at 1250, 1000 hours at 1300, and 200 hours at 1350 degrees Fahr.

(2) Will the corrosion resistance of these alloys be affected by an increase in the molybdenum content above 0.50 per cent?

We shall look forward to the completion of this investigation and hope that rupture tests at 1500 degrees Fahr. will be included.

Written Discussion: By W. K. Brown, engineering staff, Standard Oil Co., Whiting, Ind.

The authors and investigators of this subject have maintained a careful control of the principal variables, in order to determine the effect of individual elements. Their results and conclusions, consequently, do not appear unreasonable.

The oil refining industry has an interest in steels of the type under investigation, both for furnace tubes operating under corrosive and/or high temperature conditions and for oil and vapor lines. Such steels should be of a weldable quality, susceptible to grain refinement by heat treatment, and should be suitable for rolling into furnace headers. It is noted with respect to the latter item, that the majority of the steels investigated had a yield stress in excess of 50,000 pounds per square inch. Headers, into which tubes are rolled, generally have a minimum yield point strength of 40,000 pounds per square inch and consequently material for tubes should preferably have a yield strength less than 40,000 pounds per square inch in order that the tube will be deformed before the header when forming the rolled joint between tube and header.

The authors do not list any data relative to the impact properties of the steels under investigation at room and sub-zero temperatures. Such data would be of interest, particularly in the case of the steels which show the presence of

free ferrite, since some believe that the laminar structure of ferrite tends to decrease the resistance to impact. The corrosion resistance of the steels should be comparable to straight 5.0 per cent chromium and 7.0 per cent chromium, 0.5 per cent molybdenum steels, but such conclusions should be confirmed by actual tests.

In passing, it is interesting to note, whether or not there is any significance in the fact, that ferritic steel appeared in the alloys under investigation at an equivalent chromium content of 19.0 per cent. Bain has presented charts indicating that 19.0 per cent chromium-iron alloys with 0.12 per cent carbon would consist of ferrite and carbides.

The rupture strength data given in the paper for the steels at elevated temperatures are of value, in conjunction with creep test data, in indicating the factor of safety against ultimate failure for equipment designed on the basis of creep strength data, since, as shown in other papers by the authors, different classes of steels show a different ratio between the rupture strength and creep strength for a given number of hours of operation. However, for the same reason, we believe that rupture strength tests should not supplant creep tests, since the rate of creep under load is desired in many instances.

In conclusion, it would appear that the steels with vanadium additions do not have any particular advantages and that the use of the chromium-molybdenum steels will depend on economic considerations and whether or not further tests show that they have physical properties suitable for the intended service.

Written Discussion: By Jerome Strauss, vice-president, Vanadium Corporation of America, New York.

The data recorded in this paper are a distinct contribution to our factual knowledge of the properties of chromium-molybdenum-vanadium steel. Steels of this type composition, although in a number of instances of lower chromium content, have been employed for nitrided parts, for chemical plant equipment subjected to the attack of hydrogen or ammonia at slightly elevated temperatures, and for heavy forgings and machine parts of high hardness, but little of a quantitative nature has been available concerning their useful strength for high temperature applications.

Naturally, to survey an entire field, involving many variables, is a task of considerable magnitude and it seems most likely that the suggestions the writer wishes to make have already presented themselves. The authors refer to the beneficial effect of vanadium until certain percentages are reached, and the subsequent loss of this desirable effect due to further addition of vanadium. Their comparisons, however, are based upon uniformity of carbon content of the steels investigated to date. Since it is known that vanadium is an extremely powerful element in restricting the size of the gamma loop, and thus a strong promoter of unchanging ferrite, it would seem advantageous to test a series of these steels with increasing vanadium content, in which instead of constant carbon, the authors used constant microstructure in the annealed state. This means, of course, an increase in carbon content in proper proportion as the vanadium content is increased, all with the objective of avoiding the loss of a completely austenitic structure upon heating to within the heat treatment range. Other variations in composition might likewise be studied to advantage, such,

for example, as lower chromium and higher manganese contents, but the simultaneous increase of carbon and vanadium appears to be most important. It is hoped that the authors can extend their researches in this direction.

Authors' Reply

The authors greatly appreciate the discussion which has been offered to their paper and will use the many interesting points which have been raised as a guide in their future investigations on this subject.

With respect to the questions raised by Mr. Turner Smith, it should be pointed out that while certain of the steels considered were found to contain delta iron, it is not our intention to recommend these for commercial service at the present time. The results presented show that when this two-phase structure appears the strength is decreased rather than increased.

It is difficult to see how further ferrite banding could occur in these steels at the temperatures and time periods indicated by Mr. Smith. If, however, the steels are not in a completely annealed condition, and a critical amount of cold work is present, it is entirely possible that grain growth would occur in these banded areas and if this did result, the grains could not again be refined by the usual methods of heat treatment.

In regards to Mr. Smith's second comment, it is not believed that the increased molybdenum content would greatly influence the corrosion resistance in hot petroleum products but it should be pointed out that the only way in which definite information could be obtained is either through the use of A.P.I. corrosion test specimens or by trial tube installations. In other words, there is no suitable laboratory test at the present time for this purpose.

Certain of the questions raised by Mr. Brown covering the two-phase structure of some of these steels have been answered in our preceding comments. As Mr. Brown points out, it is often true that the impact resistance is lowered upon the appearance of delta iron. Impact tests have not been conducted on all of these steels and since the two-phase ones are not recommended for commercial service this test will not be conducted on them at the present time.

It is true, as Mr. Brown indicates, that most of these steels have a yield stress in excess of 50,000 pounds while headers in general have a minimum value of 40,000 pounds. We agree that the header should be stronger than the tube and it is entirely possible that through production annealing the hardness of these tube steels would be somewhat reduced. It may likewise be necessary to use headers of higher hardness for those applications requiring the use of a chromium content of 7 to 9 per cent.

A question has also been raised with respect to the rupture test replacing or supplanting creep tests. This is not our intention at all as all of our creep units are in continuous operation and, in fact, additions were recently made to the creep equipment. However, we do believe that one of the great advantages of the rupture test is its ability to more rapidly classify a series of steels of the same general type into their relative order of high temperature strength.

In this same respect, however, we do believe that the rupture test may more nearly duplicate the conditions actually encountered by the steel in cracking still service. The statement has often been made that the majority of tube

failures occur during overheating conditions and that the major portion of the bulging occurs over a fairly short-time period. If this is true, then the rate of deformation during failure is more comparable to that obtained during the rupture test and it is known that, especially with the higher alloy steels, their relative order of high temperature strength varies greatly depending upon the rate of deformation upon which the comparison is based.

In reply to the comments of Mr. Strauss we agree that the strength of the steels under consideration would probably have increased continuously with increasing vanadium content had not the two-phase structure appeared. As suggested the appearance of this phase could be prevented through a proper balancing of the vanadium and the carbon content. However, in our work we had in mind the use of these steels as seamless tubes and for this reason believed it advisable to hold the carbon content at 0.15 max. A single phase structure can, however, be maintained through the addition of austenitic formers, other than carbon, and work is now in progress on this phase of the problem.

TECHNICAL PROGRAM AND REPORTS OF OFFICERS AMERICAN SOCIETY FOR METALS—21st ANNUAL CONVENTION, CHICAGO, OCTOBER 23 to 27, 1939

FOR the benefit of members who were not in attendance at the Twenty-first Annual Convention of the Society, held in Chicago, October 23 to 27, 1939, and for purposes of record, the Technical Papers Program and Reports of Officers presented at the annual meeting are herewith published in full.

MONDAY, OCTOBER 23

Morning Session—Grand Ballroom, Palmer House

Joint Chairmen—M. A. Grossmann and H. W. McQuaid

Impact Properties of Some Low Alloy Nickel Steels at Temperatures Down to —200 Degrees Fahr., by T. N. Armstrong and A. P. Gagnebin, International Nickel Co.

The Effect of Titanium on the Macro-Structure and Grain-Coarsening Temperature of Forging Steels, by G. F. Comstock, Titanium Alloy Mfg. Co.

Introductory Study of the Nitriding of Hardened High Speed Steel by the Use of Molten Cyanides, by J. G. Morrison, Landis Machine Co., and J. P. Gill, Vanadium-Alloys Steel Co.

Some Practical Notes on High Speed Steel Forgings, by W. H. Wills, Allegheny Ludlum Steel Corp.

Morning Simultaneous Session—Room 14, Fourth Floor, Palmer House

Joint Chairmen—H. A. Anderson and J. J. Kanter

The Stress-Strain Characteristics of the Torsion Impact Test, by O. V. Greene and R. D. Stout, Carpenter Steel Co.

The Influence of Magnetic Fields on Damping Capacity, by E. R. Parker, General Electric Co.

The Interrelation Between Stress and Strain in the Tensile Test, by E. J. Janitzky and M. Baeyertz, Carnegie-Illinois Steel Corp.

The Fatigue Resistance of Steel as Affected by Acid Pickling, by G. L. Kehl and C. M. Offenhauer, Lehigh University.

Afternoon Session—International Amphitheatre

Joint Chairman—O. E. Harder and E. G. Mahin

Creep Rates from Tests of Short Duration, by J. J. Kanter and E. A. Sticha, Crane Co.

Characteristics of 5 and 7 Per Cent Chromium Steels with Varying Molybdenum and Vanadium Content, by W. G. Hildorf, Timken Roller Bearing Co., and C. L. Clark and A. E. White, University of Michigan.

Stress Corrosion-Cracking of the Austenitic Chromium-Nickel Steels and Its Industrial Implications, by J. C. Hodge, Babcock & Wilcox Co., and J. L. Miller, Armour Institute of Technology.

Ferromagnetic Austenite, by L. P. Tarasov and E. R. Parker, General Electric Co.

International Amphitheatre

Educational Lectures

The Functions of the Alloying Elements in Steel, Lecture I, by E. C. Bain, United States Steel Corp.

Visual Examination of Steels—Macroscopic Technique, by G. M. Enos, University of Cincinnati.

TUESDAY, OCTOBER 24

Morning Session—Grand Ballroom, Palmer House

Joint Chairmen—L. W. Kempf and E. F. Ross

An Analysis of Machinability Data from Cold Finished and Heat Treated S.A.E. 1045 Steel, by O. W. Boston and W. W. Gilbert, University of Michigan.

A Discussion of Leaded Steels, by F. J. Robbins and G. R. Caskey, Bliss and Laughlin, Inc.

Precipitation Hardening Characteristics of High Purity Aluminum-Copper and Aluminum-Copper-Iron Alloys, by H. Y. Hunsicker, Aluminum Co. of America.

Drawing of Aluminum, by L. J. Weber and J. T. Weinzierl, Aluminum Cooking Utensil Co.

Morning Simultaneous Session—Room 14, Fourth Floor, Palmer House

Joint Chairmen—W. E. Benninghoff and A. W. Winston

Annealing of Low Carbon Rimmed, Aluminum-Killed and Silicon-Killed Steels, by W. P. Wallace, Columbia Steel Co., and R. L. Rickett, U. S. Steel Corp.

The Prevention of Flakes by Holding Railroad Rails at Various Constant Temperatures, by R. C. Cramer and E. C. Bast, University of Illinois.

Selection of Steel and Heat Treatment for Spur Gears, by H. B. Knowlton and E. H. Snyder, International Harvester Co.

Afternoon Session—International Amphitheatre

Joint Chairmen—J. J. Crowe and R. G. Roshong

Time Quenching, by J. L. Burns and Victor Brown, Republic Steel Corp.

A Test Method for the Evaluation of Aqueous Quenching Media for Steel Hardening, by F. W. Trembour and Howard Scott, Westinghouse Electric & Mfg. Co.

Hardenability Variations in Alloy Steels: Some Investigations With the End-Quench Test, by G. T. Williams, Deere and Co.

A Hardenability Test for Shallow Hardening Steels, by W. E. Jominy, General Motors Corp.

International Amphitheatre

Educational Lectures

The Functions of the Alloying Elements in Steel, Lecture II, by E. C. Bain, United States Steel Corp.

Visual Examination of Steels—Macro Etching, by G. M. Enos, University of Cincinnati.

WEDNESDAY, OCTOBER 25

Morning Session—Grand Ballroom, Palmer House

ANNUAL MEETING OF THE AMERICAN SOCIETY FOR METALS

Chairman—William P. Woodside, President, A.S.M.

The following papers were presented by title:

The Effect of Hardness and of Temperature on the Strength, Ductility, and Toughness of a Heat Treated Carbon Steel, by S. W. Lyon, University of Illinois.

Hardness Characteristics of Some Medium Carbon S.A.E. Steels, by P. Klain and C. H. Lorig, Battelle Memorial Institute.

The Accelerating Effect of Certain Metallic Elements on Graphitization, by H. A. Schwartz, V. Fiordalis, J. L. Fisher, J. F. Shumar and M. J. Trinter, National Malleable & Steel Castings Co.

1939—Edward de Mille Campbell Memorial Lecture, by E. S. Davenport, United States Steel Corp. Research Laboratory.

Isothermal Transformation in Steels.

Chairman—R. E. Zimmerman

Afternoon Session—International Amphitheatre

Joint Chairmen—A. A. Bates and A. J. Herzig

Transformation of Austenite on Quenching High Purity Iron-Carbon Alloys, by T. G. Digges, National Bureau of Standards.

Kinetics of the Austenite-Martensite Transformation in Steel, by A. B. Grenninger, Harvard University, and A. R. Troiano, University of Notre Dame.

The Spheroidizing of Steel by Isothermal Transformation, by P. Payson, W. Hodapp and J. Leeder, Crucible Steel Company of America.

International Amphitheatre

Educational Lectures

The Functions of the Alloying Elements in Steel, Lecture III, by E. C. Bain, United States Steel Corp.

Visual Examination of Steels—Other Methods of Testing, by G. M. Enos, University of Cincinnati.

THURSDAY, OCTOBER 26

Morning Session—Grand Ballroom, Palmer House

Joint Chairmen—H. W. Graham and W. R. Breeler

Bright Hardening of Tool Steels Without Decarburization or Distortion, by J. R. Gier and Howard Scott, Westinghouse Electric & Mfg. Co.

Hardness Conversion Relations for Hardened Steels, by H. Scott and T. H. Gray, Westinghouse Electric & Mfg. Co.

Hardenability Studies on Tool Steels, by A. J. Scheid, Jr., Columbia Tool Steel Co.

Morning Simultaneous Session—Room 14, Fourth Floor, Palmer House

Joint Chairmen—L. S. Bergen and O. W. McMullan

The Nickel-Tungsten System, by F. H. Ellinger and W. P. Sykes, General Electric Co.

The Effect of Humidity of Air on the Oxidation of a Low Carbon Steel, by C. A. Siebert, University of Michigan, and H. G. Donnelly, Wayne University.

Heat Etching as a Means of Revealing Austenite Grain Size, by M. J. Day and J. B. Austin, United States Steel Corp.

The Tempering of High Speed Steel, by Morris Cohen and P. K. Koh, Massachusetts Institute of Technology.

Afternoon Session—International Amphitheatre

Symposium on Precipitation Hardening (Age Hardening) of Metals

Joint Chairmen—G. B. Waterhouse and A. B. Kinzel

Introduction to Precipitation Hardening, by Zay Jeffries, General Electric Co.

The Application of Solid Solution and Precipitation Hardening Effects in Aluminum Alloys, by L. W. Kempf, Aluminum Company of America.

Precipitation Hardening of High Purity Binary and Ternary Aluminum-Copper Alloys, by W. L. Fink, D. W. Smith and L. A. Willey, Aluminum Co. of America.

Precipitation Hardening in the Heavy Alloys, by W. P. Sykes, General Electric Co.

International Amphitheatre

Educational Lecture

The Functions of the Alloying Elements in Steel, Lecture IV, by E. C. Bain, United States Steel Corp.

Grand Ballroom, Palmer House

ANNUAL BANQUET OF THE AMERICAN SOCIETY FOR METALS

FRIDAY, OCTOBER 27

Room 14, Fourth Floor, Palmer House

Educational Lectures

The Functions of the Alloying Elements in Steel, Lecture V, by E. C. Bain, United States Steel Corp.

Morning Session—Grand Ballroom, Palmer House

Symposium on Precipitation Hardening (Age Hardening) of Metals

Joint Chairmen—Bradley Stoughton and H. P. Croft

Age-Hardening Copper Alloys, by D. K. Crampton, Chase Brass and Copper Co.

Age-Hardening of a Copper-Cobalt and a Copper-Iron Alloy, by R. B. Gordon, Westinghouse Electric & Mfg. Co., and M. Cohen, Massachusetts Institute of Technology.

Age-Hardening Precious Metal Alloys, by R. F. Vines and E. M. Wise, International Nickel Co.

Dispersion Hardening Alloys of Nickel and Iron-Nickel-Titanium, by N. B. Pilling and A. M. Talbot, International Nickel Co.

Aging in Iron and Steel, by R. L. Kenyon and R. S. Burns, American Rolling Mill Co.

Afternoon Session—International Amphitheatre

Symposium on Precipitation Hardening (Age Hardening) of Metals

Joint Chairmen—H. E. Brown and G. T. Williams

The Role of Strain in Precipitation Reactions in Alloys, by R. H. Harrington, General Electric Co.

The Mechanism of Precipitation From Solid Solution. The Theory of Age-Hardening, by R. F. Mehl, Carnegie Institute of Technology, and L. K. Jetter, Aluminum Company of America.

PLANT INSPECTION

The following companies very kindly opened their plants for the inspection of members and guests of the Society:

Tuesday, October 24

International Harvester Co., Tractor Works
Acme Steel Co., Riverdale Works
American Can Co., Englewood Plant

Wednesday, October 25

Carnegie-Illinois Steel Co., South Works
A. Finkl & Sons Co.
Lindberg Steel Treating Co.

Thursday, October 26

Mills Novelty Co.
Belden Manufacturing Co.
Stewart-Warner Corp.

Friday, October 27

Youngstown Sheet & Tube Co., E. Chicago, Ind.
Western Electric Co., Hawthorne Station
Chicago-Latrobe Twist Drill Co.

ANNUAL ADDRESS OF THE PRESIDENT

Twenty-First Annual Convention, Chicago, October 25, 1939

WILLIAM P. WOODSIDE, *President*

AS your president, it gives me great pleasure to state at this time that the Society has had a very successful year. It is in excellent financial condition, as you will learn from the treasurer's report; the membership has increased; and METAL PROGRESS is doing a mighty good job and paying its way. It is a publication of which every member can well be proud.

The Board of Trustees held four meetings during the year: November 11th, 1938, April 7th, 1939, August 25th, 1939, and October 24th, 1939. Reports of these meetings were published in THE REVIEW.

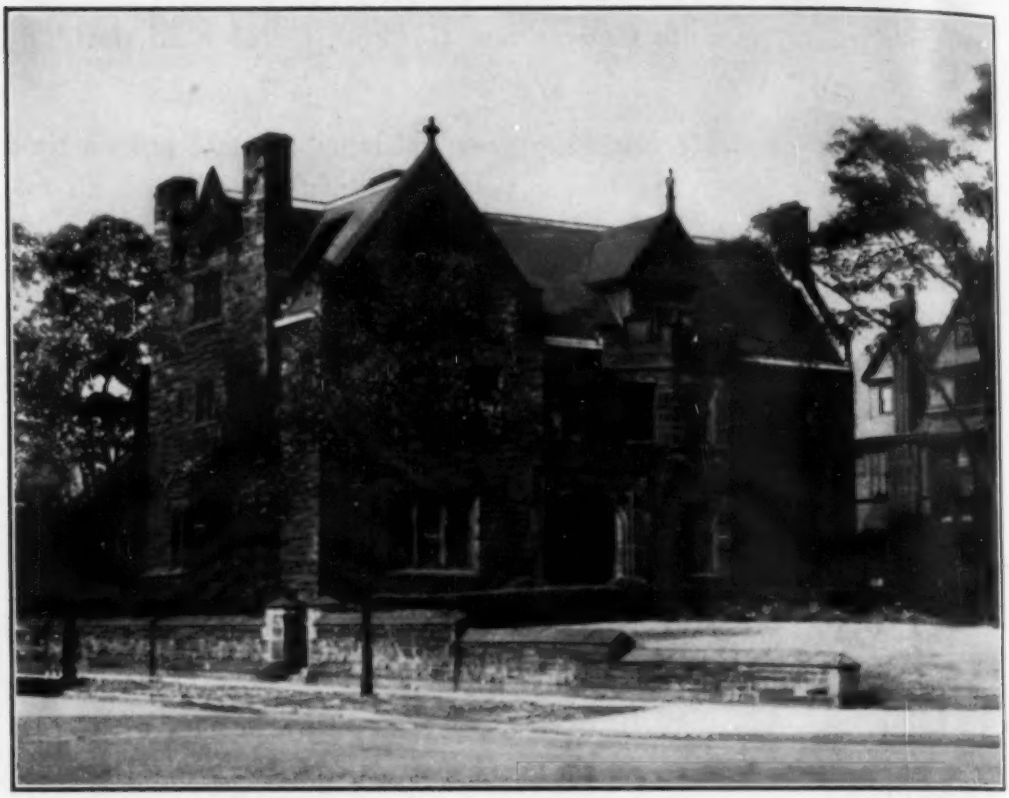
Each one of the appointed committees has carried out its duties in a most efficient and able manner. It has been a source of pleasure to me to have had such a co-operative group helping me throughout this year as your president.

I am especially glad to have my annual report carry the statement that your Board of Trustees saw fit to purchase a home for the American Society for Metals. This residence-to-be is located at 7301 Euclid Avenue just a block from the present offices and will make a permanent and dignified office, in keeping with a society such as ours.

This mansion was the residence of one of Cleveland's pioneer families in the iron ore business. The sons of this family could have sold the property for twice what they have received from us but the other bids were from commercial enterprises not to their liking. They were desirous of finding a buyer who would carry on the traditional dignity of the family residence and were happy to turn their old home over to an educational society so coincidentally related to their family business.

Thorough investigations and reports from reliable appraisers bore out our belief that the price named by the owner was an exceptionally low one considering the location of the property and the type of building.

It is a 3-story, 24-room building. The outside structure is of cut and mason-hammered stone; the interior is finished in rare mahogany, bird's-eye maple and other expensive woods, most of which were imported by the Norton family. There is a large garage



New Headquarters Offices of the American Society for Metals

in the rear of the building which at one time had been a pretentious stable with living quarters above. This building will be used for storage and handling of mailing matters of the Society.

The cost of rearranging the dwelling will be very little for its layout is well suited to the needs of the Society.

It is expected that the Cleveland office will be moved into its new home about February 1, 1940, and I feel that any member who visits Cleveland should make it a point to drop in and see what a nice, permanent home your Society has.

During the past year thorough investigations have been made by your secretary regarding an efficient employment service. Connections have now been approved by the Board of Trustees for such a service that, we believe, cannot be surpassed by any other educational society.

The new arrangement will have nation-wide connections with nearly three dozen select and well established employment offices representing us from coast to coast. Bear in mind that these employment offices are not the ordinary type but have been chosen

because of their specialty of placing men of training such as belong to the ASM. Details of this new service were published in the October issue of THE REVIEW and additional comments with reference to it will be published in later issues.

The President's Medal was presented to Dr. E. C. Bain at the annual banquet at Detroit, October 20, 1938.

The Henry Marion Howe Medal awarded to the paper of highest merit published in TRANSACTIONS during the year was awarded to Joseph Winlock and Ralph W. E. Leiter for their paper entitled "Some Factors Affecting the Plastic Deformation of Sheet and Strip Steel and Their Relation to the Deep Drawing Properties." The medal and certificate were presented at the annual banquet, Detroit, October 20, 1938.

The Campbell Memorial Lecture, established in 1925, was presented in 1938 by Alfred L. Boegehold, General Motors Research Laboratories, Detroit, entitled "Some Unusual Aspects of Malleable Iron Melting," and was published in the December 1938 issue of TRANSACTIONS.

The Sauveur Achievement Award, established in 1934, is awarded by the Past Presidents of the Society acting as a committee. The award for 1938 was presented at the annual banquet in Detroit to Harry W. McQuaid in recognition of the pioneering work he has accomplished and the inspiration that that work was to additional research upon the subject of metals. The award for 1939 will be made at the annual banquet tomorrow evening to C. S. Barrett, G. Ansel and R. F. Mehl for their paper entitled "Slip, Twinning and Cleavage in Iron and Silicon Ferrite" published in TRANSACTIONS, September 1937.

Brief mention may be made of the work of some of the national committees of the Society. The METALS HANDBOOK COMMITTEE has completed its work on the 1939 edition and most of the members have received their new edition of the METALS HANDBOOK.

What a magnificent job this committee has accomplished is evident to all, and I am sure that the entire membership joins with the Board of Trustees and your president in extending to this committee and their many co-operators our sincere thanks for their contribution to the success of the Society.

The Educational Committee during the past year has had two meetings and has prepared two excellent educational series for the present convention.

The series of five lectures by Dr. E. C. Bain on the subject, "Functions of the Alloying Elements in Steel," has been collected in book form and will be available to the members on Friday of this week.

The series of evening lectures is being presented by Prof. George M. Enos on the subject, "Visual Examination of Steels."

The sustained interest that has been exhibited in these lectures speaks well for the foresight and careful work of the educational committee as well as for the splendid work and co-operation of these two gentlemen.

I take this opportunity, on behalf of the American Society for Metals, to thank sincerely the technical societies working with us so whole-heartedly to make the Congress and Exposition a success, the American Welding Society, the Wire Association, and the Institute of Metals and Iron and Steel Divisions of the American Institute of Mining and Metallurgical Engineers.

Each year the President's Bell is presented to the chapter that your president feels has merited the honor of being recipient of it to hold for the ensuing year.

It therefore gives me great pleasure to present this award to the Cincinnati Chapter. It has carried on educational work to probably a greater extent than any other chapter. By that, I mean it has devoted more evenings for round table discussions and general meeting activities. That chapter also did a very fine job of acting as hosts to the Ohio Tri-Chapter meeting.

Before closing my remarks, I want to say that I greatly appreciate the co-operation given me by our secretary, William H. Eisenman, and the able staff he has assisting him in the Cleveland office. They have been a great help to me and I feel it would be wrong on my part if I did not publicly thank them, one and all, for what they have done to make my year as president of the American Society for Metals a successful one, which the treasurer's and secretary's reports will show.

REPORT OF THE TREASURER

BRADLEY STOUGHTON, *Treasurer*

The fiscal year ending on August 31, 1939, has been another successful year in the history of the Society and it is a satisfaction to your Treasurer to submit this report.

Our cash balance on August 31, 1939, was $100,427.42 against last year's $70,677.89.

The sale of our government securities, primarily to purchase a home for the Society, and other securities which were called for redemption have decreased our holdings of securities by 26.5 per cent. Total assets have, however, increased 10.5 per cent. Accounts receivable increased in total during the year due to an increased volume of business but an average collection period of 30 days indicates a continued healthy condition in these accounts.

The Society purchased the Norton Home on Euclid Avenue in Cleveland, a substantial stone structure, as a permanent home for the national offices, at a very favorable price of $45,000.00 against a real estate tax valuation of $42,090.00.

Inventories have remained approximately the same except the book inventory. The publishing of several new books and the 1939 edition of the HANDBOOK added nearly $5000.00 to this asset.

Although the Finance Committee, Board of Trustees and your officers have given considerable thought and consideration to investment problems, it has been very difficult to select investments for the Society account. Expert advice has been solicited and close contact maintained with our fiscal agents, the Cleveland Trust Co. At a September meeting of members of the Finance Committee and our investment counsel from the Cleveland Trust Co. our portfolio and the present investment situation were carefully reviewed and the consensus of opinion was that our investment portfolio was well diversified and had sufficient hedges, with our real estate holdings, against inflation. No suitable reinvestment of funds could be recommended at that time but it was decided that when, as and if attractive securities were available and offered, prompt action would be taken.

Our investment portfolio now shows:

		Per Cent
Real Estate (Norton Home)	$45,000.00	20.0
Public Utility Bonds	53,750.00	23.6
Railroad Bonds	36,000.00	15.8
Industrial Bonds	36,500.00	16.1
Stocks	56,000.00	24.5

As of August 31 the total cost of present investments (including the Norton Home) was $227,147.54 and the market value was $188,385.00. This market value has increased since August 31, 1939, and our reserve for market depreciation of $30,000.00 is suf-

ficient. The present market value of our securities, plus the cash on hand, is that approximately equal to the operating expenses of the Society during the past year. The interest that could be realized from this sum is of the order of 3 per cent of our current annual requirements. Therefore, the Finance Committee deems it advisable to at least maintain this figure.

The statement of income and expense for the year ending August 31, 1939, is as follows in total:

Income	$323,466.75	
Expense	275,655.39	
Net Gain		$47,811.36

Income from METAL PROGRESS decreased approximately 5 per cent this year over the prior year from	$111,769.37	to	$104,396.86	
and expense decreased 9 per cent from	109,236.82	to	99,518.86	
increasing the net gain from	$ 2,532.55	to	$ 4,878.00	

Book sales again prove to be a valuable part of our activities and show a net addition to the surplus account of over $5100.00.

The 1939 edition of the METALS HANDBOOK came off the press April 1, 1939, and as usual was in demand immediately. Income from advertising in this edition was $10,270.00. Sales for the first five months were over $6200.00 and are continuing in September and October at approximately $900.00 a month. The print order for the 1939 edition was much larger than the 1936 edition and with a larger number available for sale, after free copies are given to members, it seems that we will undoubtedly be able to balance the cost of this edition which has been covered in our 1938 and 1939 financial statements.

The 1938 Detroit Convention and Exposition was successful not only financially but also as a display of beauty and sound sales and advertising value to our exhibitors. The technical and educational value is substantiated by the increased attendance at both the technical sessions and lectures. The net addition to our surplus from the Detroit Exposition was over $30,000.00.

The membership, which is the foundation of our Society and the base for all our activities, went to a new high point this last fiscal year and reached a gross total in receipts of over $108,000.00 against totals of $105,600.00 for 1937 and $103,600.00 for 1938. Our local chapters, which have continued their splendid activities,

benefited through this increase in membership to the extent of $43,244.00.

The chapters report that they hold, in addition to the financial statement of the national office as reported above, assets of over $72,600.00, an addition of $4600.00 to the net worth reported a year ago. This substantial reserve should prove an important asset for the future activities and progress of the chapters.

CONDENSED AUDITED BALANCE SHEET
AMERICAN SOCIETY *for* METALS
As of August 31, 1939

ASSETS	
Cash	$100,427.42
Securities	153,446.02
Accounts receivable	13,876.65
Inventories	29,463.12
Other assets	6,613.71
Real estate	45,000.00
Office furniture, fixtures and equipment	8,541.60
Deferred charges	20,731.05
	$378,099.57
LIABILITIES AND SURPLUS	
Accounts payable	$ 5,497.07
Accrued taxes	867.55
Reserves	110,000.00
Deferred income	50,128.25
Surplus	211,606.70
	$378,099.57

INCOME AND EXPENSE STATEMENT
AMERICAN SOCIETY *for* METALS
Year Ended August 31, 1939

INCOME			
METAL PROGRESS—monthly publication			
Advertising		$ 98,326.50	
Subscriptions		3,933.01	
Advertisers service		1,812.85	
Sales		324.50	$104,396.86
MEMBERSHIPS			
Membership dues	$108,180.98		
Sustaining exhibitors dues	4,775.00	$112,955.98	
Less apportionment of dues to chapters		43,244.00	69,711.98
1938 CONVENTION—DETROIT			
Space rental		$ 83,275.00	
Other income		10,958.44	94,233.44
NATIONAL METALS HANDBOOK			
Sales		$ 6,208.94	
Advertising		10,270.00	16,478.94
Books published and purchased for resale			14,813.35
Interest and dividends			7,334.61
Profit on disposal of securities			4,997.90
TRANSACTIONS—bound copies, subscriptions, etc.			4,199.29
Discount earned			2,303.63
General reprints			3,039.75
Rental income—7301 Euclid Avenue			991.69
Membership certificates			241.00
Chapters—technical service			126.50
THE REVIEW—advertising, subscriptions, etc.			41.70
Miscellaneous			556.11
TOTAL INCOME			$323,466.75

EXPENSES			
METAL PROGRESS—monthly publication	$ 99,518.86		
1938 convention—Detroit	60,543.73		
National Metals Handbook	36,012.02		
Books published and purchased for resale	9,681.68		
TRANSACTIONS—bound copies, subscriptions, etc.	19,847.13		
General reprints	2,326.24		
THE REVIEW	4,595.45		
General expenses	10,127.72		
Secretary's office	12,742.21		
Chapters	7,232.66		
Accounting department	7,156.34		
Expense of trustees	2,353.18		
Expense of president	1,045.04		
National committees	1,306.20	$274,488.46	
Lectures, medals, etc.		914.96	
Books for library		180.48	
Emblems, pins and buttons		71.49	
TOTAL EXPENSES			$275,655.39
NET INCOME			$ 47,811.36

The above from Balance Sheet prepared by Ernst & Ernst, Certified Public Accountants.

ANNUAL REPORT OF THE SECRETARY

WILLIAM H. EISENMAN, *Secretary*

The American Society for Metals, on October 1, 1939, had a total membership of 10,220. Of this number 8929 or 87.3 per cent were the member classification; 638 or 6.2 per cent were sustaining members; while 630 or 6.1 per cent were juniors.

On October 1, 1938, the Society had a total membership of 9923. The membership this year showed a gain of 3 per cent over last year.

Publication Committee

The Publication Committee for the year 1938-39 was made up of the following: L. W. Kempf, Chairman; W. H. Bassett, Jr., A. L. Boegehold, J. L. Burns, John Chipman, Earnshaw Cook, R. H. Hobrock, M. Gensamer, J. J. Kanter, V. N. Krivobok, B. L. McCarthy, M. J. R. Morris, W. H. Swanger, and Ray T. Bayless, Secretary.

Throughout the year and up to the present time the Committee has reviewed and approved 50 papers, rejected 15, and is in the process of reviewing 5 at the present time, and 2 have been withdrawn by the authors.

The last meeting of the Publication Committee was held in National headquarters office in Cleveland on August 4 and 5, 1939. This meeting was concerned with the arrangements of the technical

program for this Convention. The selection of the subject for the Symposium for the 1940 Convention was deferred to a later meeting to be held during this Convention.

Transactions

There has been published, since the last annual meeting of the Society, four quarterly issues of TRANSACTIONS, i.e. December 1938, March, June and September 1939. The number of pages published in these four issues totals 1094. There were 48 papers printed together with the discussions. A total of 44,450 TRANSACTIONS has been distributed to the membership containing a total of 12,169,400 pages.

The TRANSACTIONS published since December 1938 contain papers presented at the 1938 Convention together with others received during the year.

Metal Progress

General business conditions that have been reflected in the membership totals have also influenced the advertising volume in METAL PROGRESS. For fiscal 1939 (which includes only as far as the August 1939 issue) your magazine carried a total of 816 pages of revenue advertising. The total number of editorial pages was undiminished, and the average monthly issue practically unchanged.

The Editorial Advisory Board has held three well-attended meetings, and considered a large number of problems, mostly matters of detail. The results of the survey by Market Research Corp., mentioned in this report last year, demonstrated that the membership generally approved the editorial aim and performance. The Advisory Board interpreted the survey, however, as calling for "more articles and greater diversity." Since the number of reading pages is limited the solution seemed to be in shorter articles. In 1938 METAL PROGRESS published 240 articles of average length 4.9 columns; the most frequent article was 2 columns long, of which 71 appeared. Last year (1939) there appeared 334 articles of 3.5 columns average; the most frequent length was still 2 columns, but their number had increased to 90.

"Critical Points"—editorial chats on newsy happenings—is a department that made its bow in January, and has received commendation.

That the general typographical and pictorial make-up of METAL

PROGRESS is also of outstanding excellence is proved by the receipt of First Award for Editorial Achievement in 1939 at the recent convention of the National Industrial Advertisers' Association, citing "METAL PROGRESS for the best pictorial reporting work published during the twelve months ending August 1, 1939, in the second annual competition conducted by *Industrial Marketing.*" These pictorial stories have been appearing at quarterly intervals since July 1936.

Let me take this opportunity of expressing the thanks of the Society to those hundreds of members who have contributed to the success of METAL PROGRESS by help and advice and particularly by excellent contributions to the editorial pages.

Preprints

Forty papers were presented before the 20th annual Convention held in Detroit last year. For this year's Convention 48 papers have been scheduled for presentation, 41 of which have been preprinted and distributed to those members requesting them. The total number of pages of preprints for 1938 was 792; the total number of preprint pages for 1939 is 1061. A total of 57,964 preprints have been distributed to the membership to date.

Books

Since the last Convention, two books have been published and made available to members and others, i.e., *"Hardenability of Alloy Steels"* which consists of the papers which were presented in the 1938 Symposium; and the *"Forging Handbook"* by Naujoks and Fabel. At the present time we are preparing the book *"The U. S. Patent System"* by John A. Dienner. The 5-lecture series on *"The Functions of the Alloying Elements in Steel"* which is being presented at the 1939 Convention by Dr. E. C. Bain is likewise being prepared in book form and will be available on Friday of the Convention week. The 3-lecture series by Professor G. M. Enos on *"Visual Examination of Steels"* which will be presented at this Convention will appear in book form shortly after the Convention and also the 1938 lecture series by Dr. R. B. Sosman. A series of 12 lectures presented before the Pittsburgh chapter educational course will appear in book form under the title *"Modern Steels."*

The Review

During the past year THE REVIEW has been published monthly

with the exception of July and September. Of the 10 issues which appeared from November 1938 to October 1939 all contained 8 pages with the exception of February which was 6 pages and October which was 12 pages.

The October 1939 issue was devoted almost entirely to the National Metal Congress and Exposition and had a circulation of 26,000 among the members of the co-operating societies in the Congress and other technical organizations.

Of the total space used in the 10 issues during the past year, 3095 column-inches or 75.5 per cent was devoted to editorial matter, and 1005 column-inches or 24.5 per cent to advertising. Reports of chapter meetings and educational activities used 1736 column-inches or 42.3 per cent of the total space.

Metals Handbook Committee

The METALS HANDBOOK Committee has had a very active year in the preparation of the largest edition of METALS HANDBOOK so far published by the Society.

The personnel of METALS HANDBOOK Committee, (from the time the preliminary work started) whose responsibility it was to organize and compile the 1939 edition of METALS HANDBOOK, was as follows:

R. H. Aborn
E. L. Bartholomew
A. D. Beeken, Jr.
J. P. Gill, (Chairman 1937, Term Expired 1937)
J. H. Hall, (A.S.T.M. Representative)
O. E. Harder, (Term Expired 1938)
S. L. Hoyt, (Term Expired 1938)
H. L. Maxwell, (A.W.S. Representative)
R. L. Dowdell, Chairman
C. W. Obert, (I.A.A. Representative)
G. C. Riegel, (Term Expired 1937)
A. O. Schaefer
R. B. Schenck
S. C. Spalding
Adam Steever, (Term Expired 1937)
Jerome Strauss, (A.I.M.E. Rep.)
K. R. Van Horn
J. E. Donnellan, Secretary

Although the committee held only one meeting during the year, September 23, 1938, in the National Office of the Society, the mem-

bers have handled a tremendous volume of work by correspondence consisting of organizing subcommittees, reviewing over 125 manuscripts, and making revisions in standing articles.

All subcommittees and authors were requested to review and check all articles and reports for the METALS HANDBOOK and make the necessary revisions. The revision of standing articles and the preparation of new material required 51 committees and 430 authors and committeemen for the preparation of the 1939 edition of METALS HANDBOOK. Every manuscript is submitted to a reviewing committee before given final publication approval by METALS HANDBOOK Committee. Approximately 375 members of the Society have cooperated with the Committee in this important phase of the METALS HANDBOOK program. The Committee had, therefore, a very extensive committee organization engaged in the preparation of the METALS HANDBOOK. Approximately 800 members of the Society participated in this activity for the 1939 edition.

When the METALS HANDBOOK was completed and ready for distribution on April 1, 1939, all subcommittees were retired from active work with the exception of the Subcommittee on Alloying Elements that still had an extensive program under consideration, so was requested to continue with its present program.

New subcommittees will be appointed and preliminary plans formulated for a new METALS HANDBOOK program at the next meeting of METALS HANDBOOK Committee to be held early this coming year.

The new METALS HANDBOOK contains 429 subjects, 123 of which were new for this edition, resulting in an increase of 411 pages over the previous edition. The Ferrous Section contains 229 articles with 1200 pages and the Nonferrous Section, 200 articles with 573 pages.

In addition to the two major divisions (Ferrous and Nonferrous) the METALS HANDBOOK contains 59 subdivisions arranged according to the plan proposed by R. S. Archer when he was an active member on the committee. Among those in the Ferrous Section are such important subdivisions as: general data, structure of metals, testing, heat treatment, welding, constitution of alloys, properties, technology of iron and steel, shaping and forming of metals, surface treatments, cementation processes, micrograph of iron and steel.

In a similar manner the Nonferrous Section is also subdivided

covering general data, constitution of alloys, properties, micrography, and technology of the important metallic elements and their alloys but especially aluminum, bismuth, calcium, copper, gold, lead, magnesium, lithium, nickel, platinum group metals, tin, and zinc.

Again the Society has made every effort to verify the many references in the METALS HANDBOOK to the technical literature. All references were submitted to the Engineering Library in New York for verification so that they will be of maximum assistance to the members of the Society.

By a specially appointed committee the International Acetylene Association co-operated with the Society in revising and enlarging the articles on Welding and Cutting of Metals. The committee was composed of both gas and electric welding experts and users of the processes. The work of the International Acetylene Association is greatly appreciated as their splendid co-operation with the Society has added much to the value of the HANDBOOK.

The Nonferrous Section was again under the sponsorship of the Nonferrous Data Sheet Committee of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers through a co-operative arrangement with the American Society for Metals.

As this section of the HANDBOOK contains 573 pages on 200 articles devoted to a variety of subjects on nonferrous metallurgy, it has grown to be an important section and is meeting a valuable need among the many users of the HANDBOOK. The Nonferrous Data Sheet Committee carried to a successful completion a very important program for this edition of the HANDBOOK. This co-operation is deeply appreciated by the American Society for Metals and we wish to express our sincere appreciation to the Nonferrous Data Sheet Committee and to the members of the American Institute of Mining and Metallurgical Engineers who have assisted in the preparation of the Nonferrous Section of the HANDBOOK. The personnel of the Nonferrous Data Sheet Committee was as follows:

W. L. Fink
W. E. Remmers
E. E. Schumacher
Jerome Strauss, *Chairman*
E. M. Wise
Lyall Zickrick

When the METALS HANDBOOK was ready for distribution the membership was advised of the free exchange arrangement through notices in the other Society publications and through the chapter announcements. To date 7989 members have taken advantage of

this free exchange, but there are still 2225 members of the Society who have not taken advantage of the opportunity to secure their copy.

METALS HANDBOOK is very widely used as a metallurgical reference volume. Many schools are using it in their class work. The Engineering Departments of the Government are using it as a reference volume and over 1300 copies have been distributed throughout various industries who are not members of the American Society for Metals.

Educational Committee

The Educational Committee for the year 1939 was made up of the following: R. L. Kenyon, Chairman; E. C. Bain, W. J. Conley, W. E. Harvey, H. C. Knerr, R. G. Roshong, and Ray T. Bayless, Secretary.

The Committee has held two meetings since the last Convention: one on November 1, 1938, and the second on February 8, 1939.

The meeting in November concerned itself with the selection of the two lecturers for the 1939 Convention, i.e. the 5-lecture series by Dr. Edgar C. Bain on "The Functions of the Alloying Elements in Steel," and the second, the 3-lecture series on "Visual Examination of Steels" by Professor George M. Enos. In addition to making arrangements for these two lecture series, the Committee concerned itself with a study of visual educational methods, both by means of slides and moving pictures.

As a result of a recommendation of the Committee to the Board of Trustees for suitable photographic equipment for the making of moving pictures on educational subjects, the Board authorized the purchase of suitable camera and auxiliary equipment for the use of the Committee.

A discussion and analysis of several scenarios was then held by the Committee with the result that it selected for its first motion picture endeavor the subject of "Metallic Crystals." Work has been started on the preparation of this moving picture film but it has not arrived to a state where it is ready for release.

The 5-lecture series on the *"Machining of Metals"* which was presented at the Detroit Convention has been made available in book form to the membership and any other interested parties. The second lecture series on *"Pyrometry"* by Dr. R. B. Sosman is now awaiting publication in book form.

The Committee held a second meeting on February 8, 1939, for the purpose of discussing the subjects and authors for the 1940 lecture series. The Committee decided that the subject *"Response of Metals to Various Loadings"* was a timely subject and that it was possible to select authors who were fully competent to handle the subject matter.

For the afternoon 5-lecture series the subject of *"Quenching of Steels"* was selected as that which was most appropriate and several authors were selected to handle the various lectures similar to the lecture series on the *"Machining of Metals."* Announcements will be made at a later date as to the authors that have been selected for the lecture series for 1940.

New Headquarters

The staff of the national office look forward with a great deal of pleasure and anticipation to occupying the new national headquarters in Cleveland.

The purchase of this building by the Board of Trustees represented an investment of Society funds in real estate, and as Treasurer Stoughton has said, helped to give a diversification to these investments.

We sincerely hope that members of the Society, as they travel through Cleveland, will take the opportunity to stop off and visit their headquarters.

Employment Service

We have great hope that the employment service which is just being inaugurated by the Board of Trustees is an action in the proper direction to service members and member-firms of the Society in an up-to-date, satisfactory manner.

It represents additional service to the members of the Society and its success can be measured by the extent to which the individual members and the member companies avail themselves of this proffered service.

National Metal Exposition

The present National Metal Congress and National Metal Exposition continues to serve the worthy purposes and aims for which these institutions were established. This year the Society has been particularly fortunate in that the convention and the exposition has come at a time when a business upsurge was in effect, thus affording

our members the exceptional service of having many papers of technical nature on the subject of metals presented at one time as well as having assembled in the exposition the outstanding new developments in metal production, fabrication, welding, testing, treating and inspection.

ELECTION OF OFFICERS

WILLIAM P. WOODSIDE, *President*

Complying with the Constitution, I appointed as of March 15, 1939, the following Nominating Committee, selected from the list of suggested candidates received prior to March 1, 1939:

Gordon T. Williams, *Chairman,* (Cleveland Chapter)
John S. Marsh, (New York Chapter)
Neil P. Petersen, (Ontario Chapter)
S. H. Graf, (Oregon Chapter)
G. C. Riegel, (Peoria Chapter)
R. W. Schlumpf, (Texas Chapter)
Hyman Bornstein, (Tri-City Chapter)

This Committee met at the Palmer House, Chicago, on May 19, 1939, and made the following nominations:

President—James P. Gill, chief metallurgist, Vanadium-Alloys Steel Co., Latrobe, Pa.
(1 year)

Vice President—Oscar E. Harder, assistant director, Battelle Memorial Institute, Columbus, Ohio.
(1 year)

Treasurer—Kent R. Van Horn, research metallurgist, Aluminum Co. of America, Cleveland.
(2 years)

Trustee—H. J. French, in charge of alloy steel and iron development, International Nickel Co., New York.
(2 years)

Trustee—Marcus A. Grossmann, director of research, Carnegie-Illinois Steel Corp., Chicago.
(2 years)

A report of these nominations duly appeared in THE REVIEW for May 1939.

I have been informed by the Secretary that no additional nominations were received prior to July 15, 1939, for any of the vacancies

occurring on the Board of Trustees. Consequently the nominations were closed. I shall now call upon the Secretary to carry out the provisions of the Constitution in respect to the election of National Officers.

W. H. EISENMAN: Conforming with the requirements of the constitution of the Society, I hereby cast the unanimous vote of all members for the election of the aforenamed candidates, who were nominated on May 19, 1939.

PRESIDENT WOODSIDE: The provisions of the Constitution having been complied with, I hereby declare the candidates heretofore named to be duly and unanimously elected to the several specified offices, the terms of each office just elected beginning on the day following the close of this annual meeting.

. . . President Woodside then introduced the newly-elected officers, and Mr. Gill gave a talk to the members saying he fully appreciated the honor and responsibility the office of president conferred upon him.

Mr. Woodside then presented a certificate to Dr. E. C. Bain in appreciation of his series of educational lectures on "The Functions of the Alloying Elements in Steel." He also presented a certificate to Prof. G. M. Enos in appreciation of his series of educational lectures on "Visual Examination of Steels."

Mr. Woodside then presented the President's Bell to the Cincinnati Chapter. Mr. J. B. Caine, chairman of the Cincinnati chapter, accepted the Bell, stating he accepted it on behalf of the men who did the work last year, especially Mr. Siems, who was last year's chairman.

Secretary Eisenman then presented the following papers by title:

"The Effect of Hardness and of Temperature on the Strength, Ductility, and Toughness of a Heat Treated Carbon Steel," by S. W. Lyon, University of Illinois.

"Hardness Characteristics of Some Medium Carbon S.A.E. Steels," by P. Klain and C. H. Lorig, Battelle Memorial Institute.

"The Accelerating Effect of Certain Metallic Elements on Graphitization," by H. A. Schwartz, V. Fiordalis, J. L. Fisher, J. F. Shumar and M. J. Trinter, National Malleable & Steel Castings Co.

. . . Mr. R. E. Zimmerman then took over the chairmanship for the Campbell Memorial Lecture, which was presented by Dr. E. S. Davenport, U. S. Steel Corp. Research Laboratory, on the subject of "Isothermal Transformation in Steels."

THE ANNUAL BANQUET

On Thursday evening, October 26, 1939, the American Society for Metals was host to more than 1000 members and guests at its annual banquet held in the ballroom of the Palmer House, Chicago. Seated at the speakers' table were the following: H. S. VanVleet, metallurgical engineer, American Can Co., and chairman of the Chicago Chapter; G. M. Enos, associate professor of metallurgy, University of Cincinnati, and special lecturer at this Convention; K. R. VanHorn, research metallurgist, Aluminum Company of America, and new treasurer of the Society; R. F. Mehl, director, Metals Research Laboratory, Carnegie Institute of Technology, and 1939 Henry Marion Howe Medalist; G. Ansel, metallurgical staff, Dow Chemical Co., and 1939 Henry Marion Howe Medalist; C. S. Barrett, metallurgist, Carnegie Institute of Technology, and 1939 Henry Marion Howe Medalist; O. E. Harder, assistant director, Battelle Memorial Institute, and new vice-president of the A.S.M.; H. A. Anderson, metallurgical engineer, Western Electric Co., and trustee of the A.S.M.; R. E. Zimmerman, vice-president in charge of metallurgy and research, United States Steel Corp.; Bradley Stoughton, professor of metallurgy, Lehigh University, and retiring treasurer of the A.S.M.; G. C. Kimball, executive vice-president, United States Steel Corp.; Stanley P. Rockwell, vice-president and general manager, Stanley P. Rockwell Co., and 1939 recipient of the Sauveur Achievement Award; E. C. Bain, assistant to vice-president, United States Steel Corp., special lecturer at this Convention, and past president of the A.S.M.; R. S. Archer, chief metallurgist, Republic Steel Corp., and past president of the A.S.M.; Zay Jeffries, technical director, Nela Park, General Electric Co., and past president of the A.S.M.; R. E. Desvernine, president, Crucible Steel Company of America, and principal speaker of the evening; W. P. Woodside, vice-president, Climax Molybdenum Company, and retiring president of the A.S.M.; A. E. White, director of engineering research, University of Michigan, and first president of the Society; J. P. Gill, chief metallurgist, Vanadium-Alloys Steel Co., and new president of the A.S.M.; G. B. Waterhouse, professor of metallurgy, Massachusetts Institute of Technology, and past president of the Society; J. M. Schlendorf, vice-president in charge of sales, Republic Steel Corp.; E. S. Davenport, metallurgist, United States Steel Corp., and 1939 Edward deMille Campbell Memorial Lecturer;

J. M. Ellis, general manager of sales, Bethlehem Steel Co.; A. T. Clarage, president, Columbia Tool Steel Co.; S. L. Hoyt, member staff, Battelle Memorial Institute, and trustee of A.S.M.; F. B. Foley, superintendent of research, Midvale Company, and trustee of the A.S.M.; F. J. Griffiths, president, Griffiths Bowman Engineering Co.; M. A. Grossmann, director of research, Carnegie-Illinois Steel Corp., and new trustee of the A.S.M.; D. S. Clark, instructor of mechanical engineering, California Institute of Technology, and trustee of the A.S.M.; H. J. French, in charge of alloy steel and iron development, International Nickel Co., and new trustee of the A.S.M.; L. F. Fitzpatrick, manager, Flexible Shaft Co., Ltd., and guest of honor; E. A. Terwell, salesman, Driver-Harris Co., and secretary-treasurer of the Chicago Chapter; E. T. Lawless, manager, Palmer House; W. H. Eisenman, secretary of the American Society for Metals.

Dr. Edgar C. Bain then presented Stanley P. Rockwell for the Sauveur Achievement Award saying:

"It is a pleasant assignment, Mr. President, which has been given me, to present to you the man selected to receive from you the Albert Sauveur Achievement Award. I need not recall to you the rather unusual circumstance that Professor Sauveur, himself the first recipient of the award, personally presented the plaque to the persons since selected for this honor. Our feelings of sadness that this custom is at an end are yet too keen to be referred to in words at this time. May I rather say, merely, that it is a matter of some satisfaction to us all that this Award, created by our Society to do special honor to a beloved and respected member, was established, not posthumously, but during his active days with us.

"The Committee of Award, consisting of the past presidents of the Society, have deliberated well and, to receive tonight the Albert Sauveur Achievement Award, have unanimously chosen Stanley P. Rockwell.

"The basis of award is in keeping with a spirit enunciated at the time of its creation, and I am charged by the committee to affirm that it is intended to recognize fundamental, basic contributions to the arts or technology of the metal industry, without reference to publications, or subsequent scientific extensions and study by the originator, but proven by time to have been significant and important.

"The decade prior to the World War was the beginning of a

new industrial era, an era which demanded better technical control of industrial products, and it was in this new era that Stanley P. Rockwell, after graduating from Yale in 1907, found employment in industry; first, in electrical engineering and a few years later in the physical metallurgy of steel.

"'Stan' Rockwell was born in New Britain, Connecticut. He attended Yale University and was a member of the Yale Crew. In 1907 he graduated from Sheffield Scientific School with a degree in electrical engineering. Shortly after graduation, he was employed at the Lynn Works of the General Electric Co., where he remained for about a year, and then entered the employ of the Stanley Works located in New Britain, Conn. It was at the Stanley Works that Rockwell first became interested in the physical metallurgy of steel. In 1912 he became associated with The New Departure Manufacturing Co., Bristol, Conn., taking on the duties of a testing engineer and metallurgist and it was at New Departure that Rockwell really began to hit his stride as a metallurgist.

"The New Departure Manufacturing Co., at that time, were not only making ball bearings for automobiles, but was making automobiles as well; Rockwell found himself associated here with a number of other young and enthusiastic engineers, one of whom being our past president, Frederick G. Hughes. They had difficult problems to solve but they also had the courage and determination to solve them.

"Shortly after coming to New Departure, Rockwell was given the job of supervising the hardening of ball races. The only method of checking the hardness of ball races at that time was by the use of a file. This method was far from satisfactory and Rockwell immediately realized that, to control hardness, he must have some kind of a yard stick with which to measure hardness accurately. He set about to make an appropriate tester.

"His first attempts were so discouraging that the average man would have dropped the idea. Failure, however, only acted as an incentive and those who watched him develop his hardness tester soon realized that perseverance was one of Rockwell's outstanding characteristics. It is difficult to estimate the amount of time he spent, or the great amount of work he did, during the development of his tester before he arrived at the basic principle of using both a minor and major load in measuring indentation hardness, thus giving to the hardness tester the high degree of accuracy he desired.

Around the world, the final instrument is now in use where metals are handled.

"In order to get a better understanding of what happened when various alloy steels were heat treated, Rockwell began the development of a dilatometer, so as to see if he could determine the reason for excessive distortion when encountered in hardening these steels. This first dilatometer was rather a crude affair, consisting of a dial gage, a lever system, and a quartz contact rod, assembled to a small laboratory electric furnace. From this crude instrument, Rockwell obtained valuable information as to what could happen when alloy steels were hardened. Later, he developed this dilatometer into an accurate working instrument.

"In the fall of 1916, Rockwell became associated with E. F. Houghton and Co. as their consulting metallurgist. This change offered him the further advantage of observing, at first hand, the steel problems other manufacturers had and how these problems could best be solved. He had only been with E. F. Houghton and Co. a short time when the United States entered the World War. He immediately offered his services to the Ordnance Department and was commissioned a Captain.

"Shortly after the World War, Rockwell resigned from the Ordnance Department and became metallurgist and works manager of the Weeks-Hoffman Co., Syracuse, N. Y. However, being a good Connecticut Yankee, Rockwell felt the urge to get back to his native state, and in 1920 he became metallurgist for the Whitney Mfg. Co., Hartford.

"Now for a number of years, Rockwell had the idea that he would like to set up for himself and establish a consulting and engineering service, together with a commercial heat treating shop. He knew there was a demand for service of this kind, and in 1923 he took this step and established the Stanley P. Rockwell Company, Hartford, Conn., and is still actively associated with this company as vice-president and general manager.

"Stanley Rockwell's approach to a problem is that of an engineer; he thinks along mechanical lines rather than physical-chemical lines and he is always looking for a practical solution of the problem. He has the production viewpoint—he is a hard worker because he has an active mind.

"The dilatometer has now become a rugged piece of precision equipment autographically producing both a time-length curve and

a temperature-length curve simultaneously, with heating and cooling rates under wide control.

"Not content with these achievements, Rockwell has also become a navigator, and he obtains most of his recreation and enjoyment aboard his boat, *The Chin Chin*. Sometimes it will be a fishing trip on Long Island Sound—or perhaps a cruise along the Maine Coast. Like most seafaring men, he also enjoys the thrills that go with it, even to the extent of riding out the hurricane last fall on the flooded Connecticut River.

"Rockwell is a member of the American Society for Metals, the Society of Automotive Engineers, and the American Society of Mechanical Engineers. He is still very actively engaged in many metallurgical problems and will undoubtedly make many more contributions to the art."

President W. P. Woodside then presented the Albert Sauveur Achievement Award plaque and scroll to Stanley P. Rockwell who responded as follows:

"President Woodside, Past Presidents, distinguished guests, ladies and gentlemen, and fellow members of The American Society for Metals: I accept this honor and award which you have presented to me with sincere thanks and with a profound realization that the ideas conceived by me could not have been made useful to the public without friendly aid. I am speaking now of the Rockwell Hardness Tester and the Dilatometer.

"Since college days I soon found out that metal treatment held for me a great interest. Your President has informed me that the Sauveur Award was given me for pioneer work in the development of instruments for controlling the heat treatment of steel.

"When I think back thirty years to my first responsible position with the New Departure Co., who at that time was entering the ball-bearing business and was itself a pioneer in steel treating, I was dismayed at the lack of tools for heat treatment as compared with the machine shop. Pyrometers were little known and the hardener was skeptical of them. The microscope as an aid was just coming into use, due to the far-sighted efforts of our late distinguished member, Albert Sauveur.

"The selection of steel and the processes of hardening were left to the hardener. The lack of finding the right heat for hardening and the inability to tell with any degree of accuracy or repetition the hardness of the work was a great handicap. Fortunately at the New

Departure Co. we had an enthusiastic group of technically trained men who did things, and it was under such environment that both my dilatometer and hardness tester were conceived.

"Protective patents on the hardness tester were assigned to the New Departure Co. and after leaving this company the patents were reassigned. I struggled along with but little success primarily because of funds. One of ten early machines came to the attention of Mr. Charles Wilson of the then Wilson-Maeulen Co. whose vision saw the present usage. Redesigning brought out new patentable features neglected in the first patent.

"I am telling these facts to bring out that one man alone may conceive an idea or a principle, but it takes friendly co-operation of others to build this idea into a machine of beauty, to bring it to the attention of the public, to sell it to those who have need of it, all of which creates business and employment. And for this I give all credit to Mr. Wilson and to his organization, The Wilson Mechanical Instrument Co.

"The dilatometer, conceived about the same time as the hardness tester, remained dormant until after the War. I then built working models and spent many years in development work and placed about 200 machines here and abroad. Two specific needs were found to be necessary. First a company to manufacture and sell with instrument experience and a world-wide reputation."

Robert S. Archer was then called upon to introduce Dr. Zay Jeffries for the award of honorary membership in the Society. He said,—

"On behalf of the Board of Trustees, I have the honor and the great personal pleasure of presenting to you Dr. Zay Jeffries, whom the Board has unanimously and very fittingly elected to honorary membership in the American Society for Metals. We may well be proud of the addition of his name to a distinguished list which includes Charles F. Brush, Edward deMille Campbell, Henry Le Chatelier, Elbert H. Gary, Sir Robert Hadfield, Elwood Haynes, Kotaro Honda, Henry Marion Howe, Charles F. Kettering, John A. Matthews, Albert Sauveur, Charles M. Schwab, Willis R. Whitney and Thomas A. Edison.

"Four years ago, in this room, it was my privilege to present to Dr. Jeffries, on behalf of the Past Presidents of the Society, the Albert Sauveur Achievement Award. At that time Dr. A. E. White,

in introducing Dr. Jeffries, cited his accomplishments quite adequately in view of the limited time available. This citation is now a matter of record in the TRANSACTIONS of our Society. On the present occasion I will therefore attempt to add to, rather than repeat, the things which were said at that time.

"Since our last meeting in this room in 1935, Dr. Jeffries has been elected to the National Academy of Sciences. We are very happy about this recent honor and, since we feel that Dr. Jeffries is one of us, we are also rather proud of it.

"In accepting the Sauveur Award, Dr. Jeffries very graciously sought to share the credit for his achievement with others. As one of his associates mentioned at that time, I may say that we appreciated that recognition. Tonight, however, I wish to call attention to the fact that some of Dr. Jeffries' most valuable work was carried out practically single-handed. I refer to his great generalizations on grain growth in metals, and to his important observations on the effects of temperature, deformation and grain size on the properties of metals. His laws of grain growth have been of great practical value and, with minor additions, remain some twenty-five years later a comprehensive and accurate summary of this subject. His conception of the "equi-cohesive" temperature in metals is still very useful in understanding the properties of metals at elevated temperatures.

"It is interesting to note that these researches were carried out in connection with decidedly practical studies on the manufacture of tungsten wire and the behavior of lamp filaments. It should, furthermore, be an inspiration to the younger metallurgists in particular to know that this important work was substantially completed by Dr. Jeffries before he reached the age of thirty.

"All may know of that portion of Dr. Jeffries' work which has been published. Those who have been closely associated with him also know of many contributions both large and small which have not been described in technical publications. On one occasion which was again before he reached the age of thirty, he was asked to visit for the first time an aluminum foundry engaged in the new art of making permanent mold castings. Rejections for cracks were running very high. He took samples back to his laboratory and from microscopic examination deduced the chief cause of these particular cracks and suggested a practical remedy. Again serious trouble was experienced with shrinkage in fuse bodies. Dr. Jeffries cor-

rected the trouble by inserting in the iron molds some copper plugs whose higher thermal conductivity provided the necessary increase in chill, thus permitting the successful manufacture of several million of these castings. This may seem relatively simple now, but it was new in the art at that time and was not at all obvious to others who were confronted with the same problem. I cite examples of this sort because, while Dr. Jeffries is known all over the world for his contributions to theoretical metallurgy, he is also known to his associates for his practical solutions of problems of the kind with which most of us are concerned in our daily work.

"Dr. Jeffries' contributions of a personal and individual nature did not cease when he assumed the direction of large numbers of other workers in his chosen field. To these contributions was added, however, a keen appreciation of the ideas and work of others, an unfailing enthusiasm, and an unusual ability to appraise the probable commercial value of new developments. Results have shown that his direction of research and development work has been successful, which implies that it has also been efficient. One of the principles which he recognized at an early date was expressed in the saying, 'Let the results of today determine the action of tomorrow'. In other words, he recognized the waste of money and the irretrievable loss of time which too often result from blindly following an elaborate plan of experiments without regard to the indications obtained as the work progresses.

"The American Society for Metals owes much as an organization to the efforts of Dr. Jeffries. Some of his services are indicated by the positions he has held as member of the Board, National Treasurer and Chairman of the Finance Committee, and as President. He has also contributed freely of his time and sound judgment on many occasions when he did not actually occupy an official position in the Society.

"It is indeed a privilege and an honor to present to you, Mr. President, Dr. Zay Jeffries as a candidate for honorary membership in the American Society for Metals."

President Woodside then presented Dr. Jeffries with the scroll of Honorary Membership in the American Society for Metals.

Dr. Jeffries responded to the award as follows—

"Mr. President, Mr. Archer, Ladies and Gentlemen:

"When Mr. Archer read the names of our fourteen distinguished honorary members I felt humble. When I realized that

ten of the fourteen are no longer numbered among the living, I was shocked because of the irreparable loss to mankind. On further reflection the shock was cushioned by the thought that the remaining four are still with us, and the others have made impressions on our lives which can never be erased. They live again tonight in our thoughts. Their constructive examples provide patterns for all of us to follow, and their great contributions are our valuable heritage.

"In reciting some things which I have done, Mr. Archer modestly refrained from mentioning some of the results of our joint efforts. Our names are associated, among other things, as authors of *The Science of Metals* and as promulgators of the "slip interference theory of hardening." In addition, Mr. Archer's keen and untiring mind has provided me with stimulation which I find it quite impossible to evaluate.

"The American Society for Metals is the technical society phenomenon of our generation. There must be a sound foundation for such a success. In trying to assay the building-blocks of this foundation, some things stand out clearly.

"From the beginning there has never been the thought that the Society was an end in itself, but rather the means to an end—service to its members and to industry. Members have not been asked to join to help the Society, and Exhibitors have not been asked to take space to help the Society, but to help themselves.

"It seems to me that we may truly say that the American Society for Metals represents the mass production low cost principle applied to technical society service. There is no entrance nor initiation fee to discourage potential members from joining. The dues are unbelievably low for the advantages offered, and the only qualification for membership is a desire to join.

"Again, the Society was a pioneer in bringing service to the membership through local chapter activities. These activities were financed by allocating a generous share of the membership dues to the local chapters. Of course many services, such as the publication of the METALS HANDBOOK, add to the attractiveness of membership.

"But there is, I believe, a master building-block in this sound foundation which has been largely responsible for the Society's phenomenal success. It is the harmonious marriage of the technical programs and the exhibits which we are now witnessing for the 21st consecutive year. Each complements the other. To the technical sessions come the metallurgists and other scientific workers to de-

scribe their new findings and discuss theories and practical applications. At the exhibit hall may be seen the physical embodiments of these new findings. Here also, within an area of a few acres, one can consult dozens of experts in all branches of the metal industry. The Society has not been afraid to join the technical and commercial people in its membership; it has faced the obvious situation that the technical and commercial must both be served. The meetings are essentially educational and technical, and the Exhibits are essentially commercial.

"This harmonious marriage is an example of 'emergent evolution.' This is a term coined by students of life processes to indicate the rare instances of new and unexpected favorable characteristics in hybrids. Normally, if a member pays ten dollars per year dues, he should not expect to receive services costing more than ten dollars. In the American Society for Metals he receives services costing from twenty to forty dollars. The added service is made possible largely by the Exhibit. The Exhibit is possible only because of the technical meetings. Combined, they provide an inducement for greater attendance than the technical meeting alone. Other societies join to swell the ranks. The ultimate result is that the National Metal Congress and Exposition attracts the largest gathering in the metal industry. Furthermore, it attracts the keymen. Thus does the metal industry put its stamp of approval on the service rendered by the Society.

"This solid foundation did not just happen. It is the result of much hard work on the part of many people. It reflects not only the diligent effort, but the genius of our Secretary, W. H. Eisenman. So many of our able members share the responsibility for success that they are ever on the alert to lend a helping hand to keep the good ship afloat. My own small share in the contributions of the Society to the welfare of the metal industry constitutes one of my greatest satisfactions.

"Mr. President, you know how fond I am of the Society, and you know my great personal affection for many of its members. Words cannot express my deep appreciation of this honor. May I merely say to the Society, through you, I thank you."

President Woodside called upon Secretary W. H. Eisenman to present Dr. Albert Easton White for the award of Founder Member of the American Society for Metals. Mr. Eisenman said:

"In late October 1920 I stood with a companion leaning against

the balustrade of the Singer Tower, then the tallest building in New York. We were discussing the future of the A.S.M. and how its energy and efforts might be directed towards a realization of the cherished goal the founders had visualized for it.

"'We must build well but slowly,' said my companion, Col. A. E. White, who had just been elected the first president of a newly-organized metal group formed from the Steel Treating Research Society and American Steel Treaters' Society.

"Col. A. E. White's election as president had been in recognition of his untiring efforts in gathering the discordant sections into an even symphony, and also the confidence everyone had that his counsel and advice would contribute much to the future growth and direction of the Society.

"And thus has he ever been, alert to the trend; willingly giving of his sound advice; with the interests of the A.S.M. always in his heart.

"And so, Mr. President, it seems fitting and proper that this distinguished gentleman should receive from you, the one who started the Society, October 4, 1914, a Founder Membership in recognition of his unselfish efforts in welding together the raw materials to form the base on which the present A.S.M. is built.

"Mr. President—Colonel White."

After the presentation of the Scroll of Founder Member in the American Society for Metals, Colonel White accepted as follows:—

"Mr. President, Ladies and Gentlemen:

"This honor of Founder Membership which you have seen fit to confer upon me, I accept with pleasure.

"It is a rare privilege to have been one of those instrumental in effecting the amalgamation of the Steel Treating Research Society and the American Steel Treaters' Society. That the union was wise has been borne out by the later history and success of the Society; a success which is a tribute to the continued interest, efforts and work of your officers and of yourselves as members.

"I appreciate particularly the honor of having the presentation speech made by our Secretary, Mr. William H. Eisenman, and the actual presentation by our President, Mr. W. P. Woodside. These are both men that I have known long and well; both have contributed materially to the well-being of the Society, as leaders and makers of men.

"Again, I thank you for this honor."

Following this presentation the guest of honor and speaker of the evening, Raoul E. Desvernine, president of the Crucible Steel Co. of America, gave his interesting address which is printed in full herewith.

Science and Steel in Industrial Democracy

By Raoul E. Desvernine

As a professional in the law but a novice in industry, I would have been terrified at addressing such an audience of scientists and engineers if it were not for the scientific cure which you have administered to my nervousness during the past few days. When I remarked, "How can a lawyer talk like a steel maker?" I was told, "Well, if a paper hanger can talk to the world for one and one-half hours as a statesman, you ought to be able to stick it out at a dinner for 20 minutes." Another consolation came from a person who is undoubtedly a very keen political observer. He said, "Why worry? Those in authority nowadays are not expected to know a damn thing about what they are doing or saying."

I suppose that's why I was invited to address you without any subject being assigned. Your toastmaster probably thought I was just another "paper hanger" who accidentally arrived and that he could, therefore, let me talk on any subject with authority and incompetence.

But in attending your various activities this week, I had revealed to me a subject which might be of mutual interest. I have noticed in your various scientific seminars that science is not a dry subject but, in fact, rather wet, not purely materially but somewhat spiritually, if alcoholic content is a scientific test of spirituality.

I intend, therefore, to cast aside the current nauseating jargon of jingoism and the mystical terminology of technicians and romance a little about our business. In fact, there is a great deal of romance in our business. You have got to be in business for love today to stay in it as there certainly has not been any profit in it for a long time.

I notice, however, that many have recently taken up the refrain "Happy Days Are Here Again."

Contrary to what many think, this is not attributable to the war, but entirely to the American Society for Metals. When your asso-

ciation made the metal and steel industries show off in a stockyard as they did this week, we immediately became "bullish."

And we have reason to snort and rant. The metal and steel industries have just cause to be proud of their record of achievement. They have been one of the pillars upon which the foundations of our present civilization have been built. Discoveries in the use and application of basic metals have done as much to mold and redesign our present ways of life as any other single force. The metallurgist and engineer have not only opened up new industrial frontiers but have blazed trails into new fields of economic, social and political speculation and activity. Our economic and social institutions have been fundamentally altered by scientific discovery and many of our political and industrial problems are purely the by-products of scientific progress.

The metallurgist and chemist in his laboratory and the engineer in his experimental workshop are dynamic political and social forces. They must, therefore, not be unmindful of the cultural and spiritual effects of their physical discoveries. The genius of the radio is not in its mechanical composition but in the effect it has had on the entire intellectual life of the world. This is but one isolated illustration. If we reviewed all scientific progress for the past 40 years in relation to its effect on our daily lives and thinking, we would be graphically reminded that the metallurgist, chemist and engineer have completely changed the pattern of human life, and will, in the future, continue to change it more radically than any politician, college professor or economic royalist. The germ of a new civilization is found under the microscope more often than in the bombastic speeches and clever maneuvers of statesmen and soldiers. Newly discovered uses of natural forces and resources release new economic and industrial forces which in turn create new political and social problems. We live in an integrated universe. Every sound wave released here reverberates around the world.

And, on the other hand, scientific discovery may not only be a great benefit to the human race but it can also be destructive of the human race. It all depends upon the use which human beings make of their discoveries. The folly of man, not the intention of the scientists, is responsible for the destructive use of the agents employed in modern warfare. The ultimate value of invention depends entirely upon the thinking of Men. As a Man thinks, so he becomes; as Men think, so Society becomes. We must, therefore, wage a

battle of ideas and, for this war, you scientists are especially well equipped.

We must not be distracted from our domestic problems by foreign war. A war of insidious propaganda is being waged against our traditional and basic political and economic institutions. We can only meet this challenge with straight thinking and publicized facts.

Let us tonight scientifically counterattack a few of these malicious attacks on industrial democracy.

On the Political Front—In the last decade we have witnessed throughout the world, and to a significant extent in our own country, unprecedented assumption by government of political controls over all economic and social activities. Our forefathers designed a political system on an economic and social structure in which individual freedom could live. They sought the liberation of the human spirit so that man could design the pattern of his own culture and work out his own economic destiny through his own ingenuity and free enterprise. They did everything conceivable to constitutionally guarantee us against the economic strangulation caused by the tightening hand of government on individual liberty and free enterprise. They emphasized the overwhelming importance of spiritual and intellectual freedom. It is interesting to note that our Federal Constitution contains more denials of and limitations on the powers of government than it does grants of power.

Our founding fathers indeed had a scientific attitude toward government. Scientific progress can alone flow from striking the shackles off the human mind and setting it free for adventures into the uttermost realms of space and into the boundless energy imprisoned in an atom. Furthermore, according to his nature, man must be free to use and enjoy the conquests of his adventure and he must have the urge to continue and pursue his voyages of discovery by not being deprived of the rewards of his exploits.

Time does not permit my detailing all of the shackles which have been imposed upon us in the fair name of modernization and under justification of emergencies but I can assure you that practically every basic productive, distributive and financial agency of our commercial life is already subject to some government control. The instrumentalities for the communication of information are also already under governmental supervision.

This new ideology of a totalitarian paternalistic state, which has

captured most of Europe and which has been creeping up on us here by subtle insinuation, is anti-scientific. I say it is anti-scientific because it harnesses the free play of human ingenuity and curiosity; it destroys the urge in man to risk new voyages of discovery in the hope of reward; and it curtails creative experience. In fact, it is anti-man, as it seeks to recreate man in a new image according to some economic formula which is antipathetic to his nature. We are not just fussing about political forms and economic formulae; we are fighting a philosophy of life.

In my opinion, war would temporarily, if not permanently, sound the death knell of the free enterprise system. Bear in mind that the European combatants, even the so-called democratic states, are not fighting this war under the free enterprise system.

Industry, as well as man, is mobilized and regimented in war. Even in preparation for a possible war, our Government has formulated most comprehensive plans for industrial mobilization. These plans, if carried out, would completely alter our industrial processes and distort our whole national economy.

War profits are a thing of the past and the proverbial "munitions' maker's wife" will be a shabby creature in the next war. Let no one tell you that business men want war! I know what participation in this war would do to American business. And I am skeptical that even neutrality might prove disappointing.

All of us seem, however, to be very conscious of what participation in the war might mean to us; but few of us seem to appreciate the real import of neutrality.

The preservation of modern neutrality seems to require a wider use and expansion of governmental controls. There are a great number of business-control laws now on the statute books but largely forgotten because they have not been used since the last war or because they were enacted for some emergency not usually associated with war. They confer drastic powers on the president and could be put into operation on a moment's notice. Other controls may be legislated. We may at least be certain that we are already in a period of an increased governmentally manipulated economy. Let us not be too sure of a "war boom"! It might prove to be a "war bomb"!

Furthermore, you are trained to discover, isolate and evaluate facts and the relation of facts to facts. You accept demonstrated conclusions regardless of preconceived notions. A scientist rational-

izes; he never emotionalizes. In a word, you weigh and judge problems scientifically—with the head and not with the nervous system and the passions.

The scientific approach to political and economic problems is imperative. The scientist belongs in politics because politics has already intruded itself into science.

Scientific freedom will not prosper under political slavery. To be a scientist you must be intellectually free. Therefore, if you believe in science, you must resist all attempts to curb or harness human freedom and you must fight on the political front in defense of democracy.

On the Social and Economic Front—As scientists you must also fight on the economic and social front of industrial democracy, the free enterprise system. Its enemies are trying to destroy it by a spread of false propaganda. You must refute this false propaganda with facts.

You are not doing your duty to your profession if you continue to permit the impression to grow that scientific progress and the mechanization of industry produces unemployment, that machines displace men. This is simply not true! Let's look at the record for a moment.

The period between 1900 and 1939 is the period of the greatest improvement in the mechanization of the productive processes in the history of the United States; so that is certainly the period which we should examine to test the truth of this accusation.

During that period, the population of continental United States increased 70.8 per cent.

The average number of wage earners in the manufacturing industry during that period increased 111.2 per cent and in blast furnaces and steel works and rolling mills, 125 per cent. *This proves that jobs increased faster than the population.*

Furthermore, since 1900, the amount of steel in use in this country has increased nearly 17 times as fast as the nation's population, in spite of the fact that improved technology in both the manufacture and use of the steel in the past 20 years has greatly increased the life of steel in service. Per capita consumption of steel increased 650 per cent. So consumer demand increased phenomenally.

Now let's see what happened to wage rates and hours of work!

Average hourly earnings in the manufacturing industry increased 191.9 per cent and in the steel industry 227 per cent. The

average weekly earnings in the manufacturing industry increased 100.1 per cent and in the steel industry 108.1 per cent. On the other hand, the average hours of work between 1914 and 1939 (the only period during which there are authentic figures) *decreased* in the manufacturing industry 32.2 per cent and in the steel industry 41.8 per cent. Production per man hour increased 126 per cent.

It is, therefore, apparent that jobs grew faster than population, that actual earnings increased with a greatly reduced work week and production per man hour increased. On the record, machines have not displaced men and decreased gainful employment!

We, who invent, produce and operate machines, cannot afford to let this fetish continue that mechanical progress is *anti-social.*

Idle machines, not *busy* machines produce unemployment. And you can't blame idle machines on Big Business, as only busy machines can make profits.

The Steel Industry may be proud of its wage record. From an average wage rate of 24.5 cents per hour over the period 1890-1915, it has risen to 82 cents in 1937-1938 and this rate is 27 per cent higher than the average wage paid in all manufacturing industries. And bear in mind that employment in 1935 was only 3 per cent below 1929 although steel output was 49 per cent lower. Furthermore, out of every dollar which the industry received in 1929, 35.5 cents went into the pay envelope of employees. Each year the employee has been getting more. In 1937 he was getting 37 cents and in 1938, 40.5 cents.

And here is one of the most challenging facts of all! The purchasing power of the hourly wages of each worker in the steel industry has increased 55.8 per cent over that great year of 1929 to which everyone still looks back with envy. This figure takes fully into account changes in the cost of living. And if someone observes, "Yes, but hours of work have been reduced so that weekly income in the wage earner's pay envelope is less"—you may reply, "Certainly, but even taking this into consideration, his weekly earnings in 1939 have increased in purchasing power over 1929 by 2.8 per cent and you can't blame reduced working hours on the employer."

And from 1923 to 1929, the average composite price per pound for finished steel was 2.35 cents and in 1938, 2.30 cents per pound or 2 per cent lower. So even the consumer has benefited.

Why shouldn't we be justly proud of our industry's record? We have withstood the distortions and maladjustments of the years

of economic depression—the aftermath of the last World War—with fortitude and success and to the benefit of our wage earners and customers but at the expense of our security owners. We have conducted vast research, modernized and expanded plants and have made great technological progress through all that depressing period.

It seems to me that our industry needs to yield to no one on the economic front. We are better equipped and manned today to "do our bit" than ever before, and it is the metallurgist and engineer who have principally made this possible.

In addition to these contributions to our economic and industrial life, steel has also contributed to the safety of human life. Mechanical failures have been greatly decreased as a result of the increased uniformity and strength of steel. Sanitation in many of our food and beverage preparations and dispensing units is constantly guarded by stainless steel. The utilization of the superior strength of steel has made travel in our modern automobiles and railroads safer. The highly successful operation of our modern air transport lines is principally a function of the steel industry's ability to produce strong steels, but steels practically free from imperfections. New magnet steels have revolutionized magnetos and loud-speakers and foreshadow a new era in radio communications. Entire new industries, with new opportunities of work for thousands, have been created as a result of metallurgical discoveries. Hard labor has become less and less burdensome and physically depressing.

It is impossible in my limited time to do more than high-light a few advances made by the metallurgist and engineer in our industry on the social and economic front but the few selected illustrations conclusively demonstrate that you have not been "anti-social" as so many crackpots unchallengingly claim. You have probably not been as "social-minded" as these political magicians but you certainly have been more "socially effective"; and action speaks louder than words.

Technological progress always means economic and social progress. And, do you realize that American industry is estimated to spend around $200,000,000 a year in research alone? Only great aggregations of capital can afford such an outlay for research. Moreover, corporations make staff research by numerous co-ordinated experts possible, which is impossible in individual business and direct research along specified practical lines, as against abstract types of research in great universities.

Now a word as to the future! And in this I am only echoing what I have heard you say.

Although the metallurgist never prophesies spectacular discoveries of new products, he, nevertheless, knows that research laboratories are strange places where the unexpected is always happening, and no one can be emphatic in stating that the day of sensational new products is past.

You can make a needed contribution by furthering a movement towards simplification and standardization of products, by finding ways of securing equal properties with a lower alloy content, by making large sections of steel with equal strength all the way through, by developing better tools and better dies and by producing quality steels with a high degree of reproducibility.

The field of greatest profit lies in the reduction of production costs with improved quality and wider applications and consumer uses. These must be the discoveries of the scientist; so you are the most potent economic force in the industry. With taxes and labor at "frozen" levels, we can alone profit by reducing our direct production costs and these production costs are basically scientific problems. You have won our battles for us on the social and economic front thus far and we look to you for leadership in the greater battles which confront us.

It has been interesting, during the past ten years, to see the gradual change from dependence on the research of Europe to supply the American metallurgist with the clue as to how to improve his product or how to synthesize alloys in a new way to secure a superior product. The American metallurgist is slowly but gradually taking over from the European metallurgist the work of establishing the fundamentals involved in steel making, steel treating, and steel use. Since the last war, the realization of the importance and control of grain size in steels, a fundamental understanding of the mechanics of hardening and softening, and the importance of slags in melting practice have all been contributions of American metallurgy. This is strong evidence that the American metallurgist is tackling his problems more practically and fundamentally and is, therefore, making a more direct contribution to the scientific foundation of steel making.

We no longer have to rely on European sources of supply of metallurgical knowledge and skill. We can "carry on" with our own metallurgical "resources." It is about time that we stopped our

idol-worshipping of "Made in Germany" and began to boast of "Made in America."

And so as I survey our industry as a newcomer who does not "fail to see the trees because of the forest," I can boldly state that *on its record* it has justified itself as a real constructive and progressive force in our economic progress and that it has contributed greatly to social and humanitarian advance. We owe it to our industry and to our country to become active scientific propagandists in correcting the false impressions that the rank and file have been given of our industry's record in our national economy. If industry is to be expected to go "over the top" it must have the sympathetic understanding of the voters as it is the voters who make and control our government. The way to change government is to change individua' opinion; that is your and my job.

Political democracy and industrial democracy go hand in hand. You cannot have political independence and industrial dependence; nor can you have industrial independence and political dependence. Political freedom and industrial freedom are each only inseparable component parts of *human* freedom. The attainment of human freedom, as I have said, comes alone from liberating the human spirit so that man can design the pattern of his own culture and work out his own economic destiny through his own ingenuity. This is a scientific fact, a natural law; it is integrated in man's very nature.

We must, therefore, "de-bunk the modern bunk" that industry has been *anti-social, anti-democratic;* that is pure nonsense which cannot successfully survive the challenge of facts. It is our duty to destroy this modern heresy.

We are faced today with a world challenge to the fundamental concepts of our civilization and I am confident that industry can and will demonstrate by its achievement that political and industrial democracy is the only practicable way of life and that it is workable under *all* and *any* conditions.

There are new frontiers in America which hold the promise of greater wealth, more goods, more jobs and a higher standard of living than ever produced by territorial conquests and trade domination. These peace time frontiers stem out of the shops and research laboratories of industry. You are the masters of our industrial destiny!

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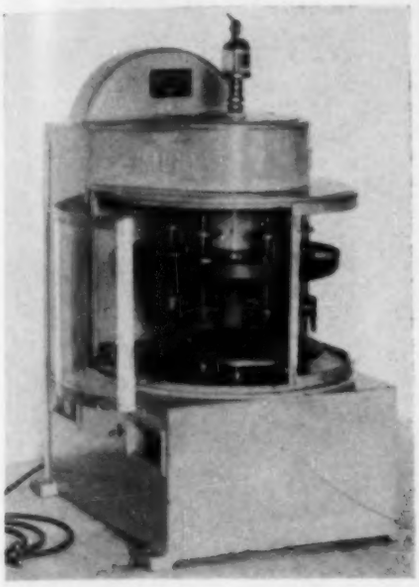
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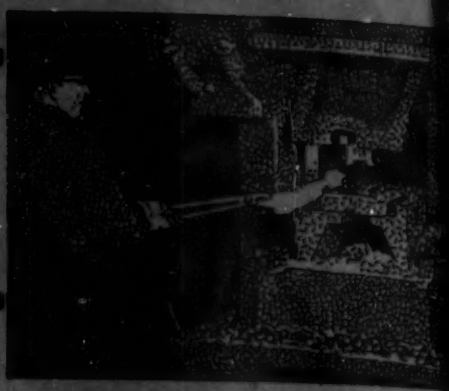
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